

FABRICATION OF AN OXYGEN SENSOR AND ITS APPLICATION TO INVESTIGATE IRON ORE-CARBON REACTION

By
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DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR

FABRICATION OF AN OXYGEN SENSOR AND ITS APPLICATION TO INVESTIGATE IRON ORE-CARBON REACTION

**A Thesis Submitted
In partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY**

**By
AVINASH KESHAV GOKHALE**

to the

**DEPARTMENT OF METALLURGICAL ENGINEERING
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C E R T I F I C A T E

Certified that this work on "Fabrication of oxygen sensor using solid electrolyte technique and its application for the investigation of the iron ore-carbon reaction" has been carried out under my supervision and that it has not been submitted elsewhere for a degree.

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This thesis has been approved
for the award of the Degree of
Master of Technology (M.Tech.)
in accordance with the
regulations of the Indian
Institute of Technology Kanpur

Dated: 78 8 24

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEWA) Objective of the work:

Oxygen sensor based on solid electrolyte cell is a versatile device in measuring and monitoring the oxygen concentration in gases or liquids. The response of the sensor to the change in oxygen concentration is very quick (less than 1 sec.) and the range over which it can be used is very wide. This sensor can be employed for chemical analysis of some gas mixtures as well. Due to these outstanding advantages, the use of this sensor on the commercial scale for various applications is coming up fast in the industrially advanced countries. Since this has not become a common feature in India, it was planned to fabricate an oxygen sensor for gases only, to test^{hh} its performance and to use it for laboratory investigations.

The reaction between iron ore and graphite is an important reaction in blast furnace and also in the rotary kiln process of sponge iron making, which offers an important alternative method for iron production. The course of such a reaction can, in principle, be followed by measuring the rates of generation of CO and CO₂. The latter could be determined by monitoring the flow-rate of the gas mixture coming out of the reaction chamber and analysing its CO/CO₂ ratio by the solid electrolyte oxygen sensor. Therefore it was chosen for investigation.

B) Literature Review:B-1) Solid Electrolyte Oxygen Sensor:

The review shall be restricted to sensors to be employed

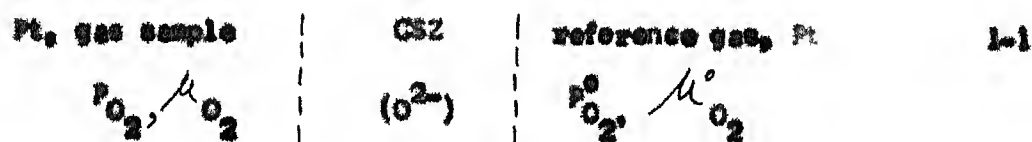
for gases.

Solid electrolyte, are solids which allow ionic conduction only. For the oxygen sensor the materials which conduct oxygen ions are of interest. Again the ionic conduction should be very close to 100 pct. if it has to be useful as an electrolyte in a galvanic cell. For this $\text{ZrO}_2\text{-CaO}$, $\text{ZrO}_2\text{-MgO}$, $\text{ZrO}_2\text{-Y}_2\text{O}_3$, $\text{ThO}_2\text{-Y}_2\text{O}_3$ have been employed. But calcia stabilized zirconia, $\text{ZrO}_2\text{-CaO}$ (CSZ in abbreviation) is the most important one.

A number of review articles have already appeared in the literature (1-4). Therefore the following discussion would be brief.

B- 1-1) Principle of operation of oxygen sensor:

Using the CSZ, an oxygen concentration cell is formed as shown below.



$$\text{For this cell } E = \frac{\Delta G^0}{2F}$$

$$\therefore E = \frac{RT}{2F} \ln \frac{P_{O_2}^0}{P_{O_2}} \quad (1-1)$$

$$= \frac{T}{20.169} \log \frac{P_{O_2}^0}{P_{O_2}}$$

where E = emf in millivolts

T = Temperature in $^{\circ}\text{K}$.

F = Faraday constant

R = Universal gas constant

P_{O_2} is determined from measurement of E and T since $P_{O_2}^0$ is known.

If the gas contains, besides oxygen and inert gas, any species reactive to oxygen such as H_2 or CO , then an equilibrium similar to the following prevails, since solid electrolyte cells are operated at high temperatures only



$$\text{and } P_{O_2} = \frac{1}{K_H} \left(\frac{P_{H_2O}}{P_{H_2}} \right)^2, \quad (1-3)$$

where K_H is the equilibrium constant of reaction (1-2).

Therefore measurement of P_{O_2} allows determination of P_{H_2O}/P_{H_2} ratio in a gas since the value of K_H can be calculated from the known standard free energy of formation of H_2O .

Similarly if the gas contains CO and CO_2 , P_{CO_2}/P_{CO} ratio can be determined. Knowing the total pressure, P_{CO} and P_{CO_2} can be calculated individually.

The above examples illustrate as to how the oxygen sensor may be employed for gas analysis.

Over years many methods are being used for oxygen analysis in gases such as Orest apparatus, spectrometry, gas chromatography etc. But the discovery of the concentration cell using solid electrolyte has led to a very successful breakthrough in oxygen concentration measurement in various phases. The outstanding advantages are:

1. Ref response is specific, rapid and continuous.
2. Ref measurement can be done without disturbing the system.
3. Single sensor can be used over wide ranges of oxygen concent..

and temperature.

4. The cell voltage is amenable to high precision measurement.
5. It can be used for the system not containing oxygen also since it measures oxygenizing potential as such.
6. CSZ is excellent ceramic material and stands high temperatures.

There are some inherent limitations also

- 1) It can not be used below 500°C because of high resistance and irreversibility.
- 2) It has a poor thermal shock resistance.

B-1-II Some basic considerations

Since both the electrodes are gases, there is a need to separate them completely. It can be done in two ways as shown in figure 1-1. Generally platinum is used as lead wires. It is suitable because of its low reactivity and high melting point. Its surface quickly attains equilibrium with respect to gaseous phase. Rh , Ir , Ru etc can be used but are costlier.

B-1-III Leakage of oxygen

One problem with solid electrolyte is the leakage of oxygen from reference to the sample gas side (or vice versa) through pores or due to electronic conduction in solid electrolyte. The latter is the predominant mechanism of leakage (5), and it increases sharply with temperature.

When oxygen concentration in inert gas oxygen mixture is measured, especially at low oxygen concentrations, this leakage of oxygen may lead to considerable error in measurement. So to keep the

error within limit, one has to increase the flow of the gas mixture in order ^{to} make the influence of leaked oxygen negligible.

If there is a leak of 4×10^{-5} cc/sec. at 1200°K , with pure oxygen as reference, in order to cut down the error to less than 4% the flow rates of the Ar-O_2 mixture should be at least 0.1, 10, 10^3 cc/sec. for P_{O_2} values of 10^{-2} , 10^{-4} and 10^{-6} atmospheres respectively. This means that reasonably accurate measurement is possible upto $P_{\text{O}_2} \approx 10^{-4}$ atmospheres only (5).

Instead of inert gas oxygen mixture if CO-CO_2 or $\text{H}_2\text{-H}_2\text{O}$ mixture is present, then the buffering capacity of the gas is considerably enhanced. The leaked oxygen reacts with H_2 or CO forming H_2O and CO_2 respectively. Since the change in the concentration of CO_2 or H_2O is very small, it does not change the CO/CO_2 or $\text{H}_2/\text{H}_2\text{O}$ ratio appreciably so even for very low oxidizing potentials reasonably low flow-rates may be employed.

B-1-IV Operating temperature range:

At low temperature, resistivity of the electrolyte is high and irreversibility sets in the electrode reaction. Moreover the contact between the Pt-electrode and the solid electrolyte becomes poor. The minimum operating temperature is held to be 400°C by various investigators.

At high temperature, leakage rates are highly enhanced, electronic conduction increases and volatilization of platinum as oxide begins. The construction and maintenance of the assembly also becomes difficult. The upper temperature reported so far is $1100^\circ\text{--}1150^\circ\text{C}$

B-1- V Measurement of the cell emf:

The emf E in the equation (1-1) is the open circuit emf in ideal case. So no current should be drawn while measuring the cell emf. Otherwise the reading may be considerably erroneous. So measurement is done with high impedance voltmeter. The minimum input impedance is about one megaohm.

B-1-VI Industrial applications:

Two approaches are possible regarding the use of oxygen sensor. It may be directly introduced into the reaction tube or furnace and direct measurement be made. Alternatively, it may be kept as separate instrument with its own heating arrangement. Latter is preferable since it increases the life of the sensor because of absence of thermal shocks, mechanical and chemical damage etc. Moreover it increases the accuracy since its design can be made sophisticated.

So far this kind of meter is primarily being put to monitor and control the gas composition than to make accurate measurements. It is being used in combustion control, basic oxygen furnace, annealing of metal products, analysis of flue gases in blast furnace, the generation and control of carburizing atmosphere etc.

Few commercial designs have also come up, some of which are the following.

1) Westinghouse oxygen analyzer (6)

Some of its applications are

- a) Measurement of oxygen impurities in high purity gases.
- b) Chemical plants: Inert gas blanketing control Control and measurement of oxygen concentration in feed streams.

c) Food Industry: Inert gas blanket monitoring over vats, processing vessels and for industrial safety.

2) Use of oxygen sensor in combustion control of the furnaces: (7)

It senses the oxygen concentration in the furnace flue gases and provides a corrective signal for furnace combustion control.

3) Pulmonary function oxygen monitor⁽⁸⁾.

This is for the medical applications. It provides a direct read out of the oxygen concentration in each inspiration-expiration cycle. The oxygen concentration is accurately recorded ($\pm 1\%$) on a moving strip chart which even depicts a variation caused by the heart beat during expiration. Its typical applications are:

- a) Continuous monitoring of post cardiac surgery patient
- b) respiratory efficiency in the post-operative patient
- c) Study of the cardiovascular system through the effect of exercise upon respiration.

B-2 Reduction of Iron Ore by Carbon:

It was recognized even in early days, that kinetically, a solid-solid reaction is expected to be much slower compared to a gas-solid one since solid-solid contact area is much smaller compared to gas-solid contact area and solid-state diffusion is much slower compared to mass transfer in gases.

Several investigators (9,10,11) attempted to measure the rates of direct reduction by continuous evacuation of the chamber in the temperature range of 700-1150°C and pressure range of 5×10^{-4} mm.

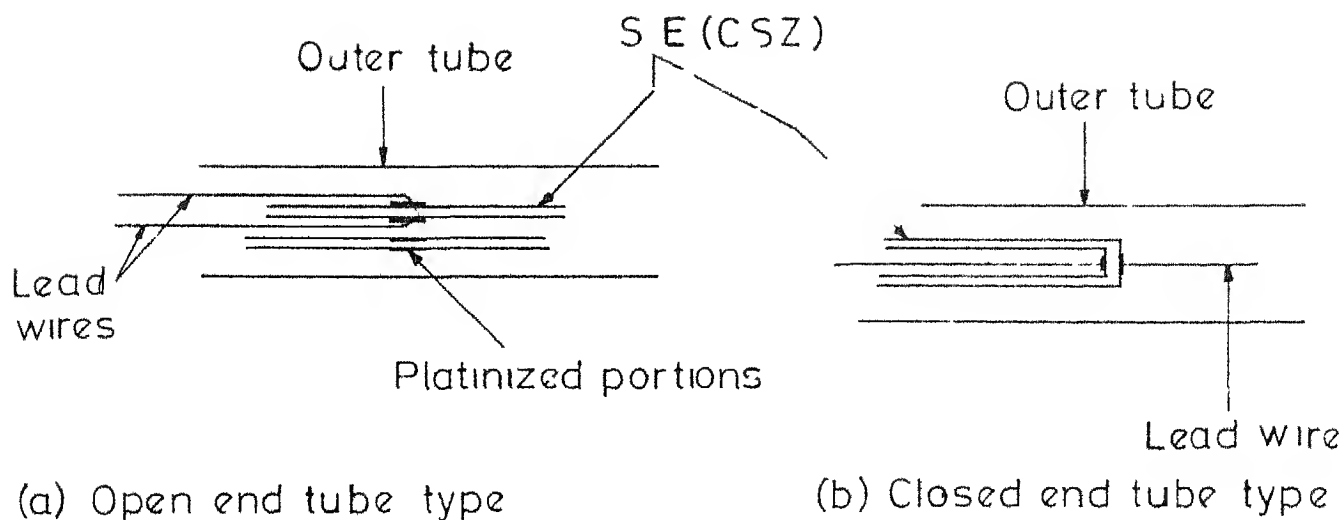


FIG 11

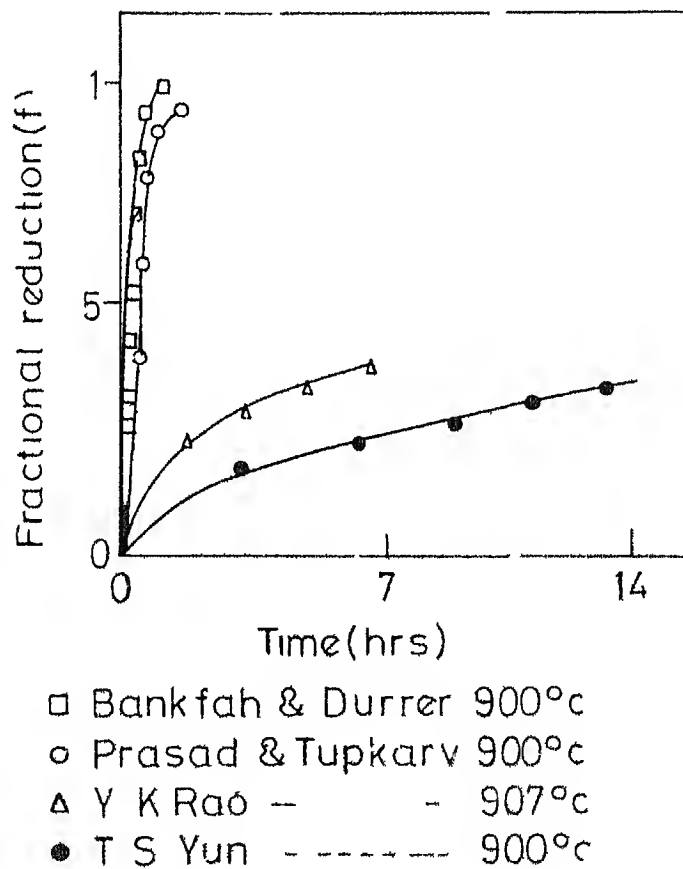


FIG 12

10×10^{-4} torr. They assumed that the gas phases were substantially eliminated by evacuation and hence reaction rates obtained represented those of solid-solid reaction. These results were compared (12) with the experimental data obtained by Y.K. Rao (13), who employed inert gas flushing and that of Baldwin (14), who passed nitrogen over the heated bed of iron oxide and coke.

Results are shown in fig. (1-3). It may be seen that the rates under inert gas flushing were even smaller compared to those obtained under evacuated conditions. These discrepancies were explained by Abrahams and Ghosh (12) in the following way. Flow of gas through a pore is 'Knudsen' when the mean free path is larger than the pore diameter. This condition is very well met in the tiny pores of pellets under the reduced pressure. So although the chamber was evacuated the pressure inside the fine pores of the pellets were likely to be appreciable, because flow of CO and CO_2 from the interior of the pellet to the chamber would require a substantial pressure.

Reduction of iron oxides by carbon occurs in the following two stages.

Reduction of the oxide viz.



and gasification of carbon, viz



First of all the salient kinetic features of these two stages will be presented.

B-2-1 Kinetics of reduction of iron oxides by carbon monoxide

Some investigators studied the reduction kinetics of FeO . Both single-pellet and thermobalance technique (15, 16) as well as packed bed systems were employed (17, 18, 19). The temperature ranged from 700°C to 1200°C and both CO as well as mixtures of CO and CO_2 were employed. The particle size ranged from a fraction of a millimeter to 4 centimeters.

At low flow rates of CO or CO-CO_2 mixtures the rates of reduction were found to depend on the gas flow rate and increased with the increasing flow rate (16, 17, 18) till there was no more influence. At this stage, reagent starvation as well as mass transfer in the gas phase has significant influence on the reduction rate.

It was observed that the following equation is applicable for the reduction of iron oxides by CO (13):

$$1 - (1 - f)^{1/3} = Kt \quad \text{.....} \quad (1-4)$$

where f = fractional reduction = $\frac{\% \text{ Reduction}}{100}$

t = time

and k = constant.

For chemical control, K of equation (1-4) should be inversely proportional to the diameter of the specimen. This was observed in some cases (20) but Eickensen and Clarke (18) found it to be independent of the size of the specimen. Khalafalla (19) found a marked prompter action of impurity oxides on the reduction of small Fe_2O_3 particles (-4 mesh to plus 5 mesh) by CO . The extent of reaction rate enhancement was proportional to the ionic radius and

electronic charge of the promoter additive. This pointed out to chemical control.

The values of activation energy were variously found as 8.5 Kcal/mole (15), 13.9 Kcal/mole (18), 33-50 Kcal-mole (19) Khalafalla (19) found an unusually large activation energy (30-50 Kcal/mole) for reduction of coarse and crystalline FeO and Fe_3O_4 . He attributed it to a large negative heat of adsorption of CO on the oxide surface.

It is recognized that the reduction process is complex. Such complexity arises from various sources. The product layer is porous and the diffusion process through the pores is influenced by the pore texture, which again depend on a number of factors. In addition, swelling of pellets, cracking during reduction, recrystallization of the reduced iron layer and the presence of unreduced iron oxide islands add to the complexity further.

B-2-II) Kinetic aspects of gasification of carbon by CO_2

Cokes, carbon and synthetic graphites are highly porous with pores ranging from about 10 \AA^0 to several microns in diameter. The kinetic steps involved are gas film diffusion, diffusion through pores and chemical reaction at the gas-solid interface. It has been established that the chemical reaction is exclusively rate controlling below 1100°C , if the size of the graphite is not too large (diameter less than 1 cm.) such a conclusion has been arrived at from evidences such as high activation energy (80-90 Kcal/mole) and strong influence of solid and gaseous impurities even in trace quantities.

The rate of gasification decreases enormously with increase in percentage of CO in the gas. The rate with pure CO_2 at 1 atmosphere has been found to be 100 times larger compared to a gas of 90 percent CO- 10 percent CO_2 at 900°C (21).

In presence of catalyst the activation energy of the gasification reaction has been found to be as low as 15 Kcal/mole (22).

Walker and co-workers (23) found that the iron is an effective catalyst only when it is present as metallic iron mixed with a little FeO . The explanation put forward contends that the oxygen transfer at the graphite surface is enhanced by alternate oxidation of Fe and reduction of FeO . The catalytic activity is helped by mobility of oxygen on the metal surface. Ni and Co also exhibit similar catalytic action.

B-2-III Kinetic aspects of reduction of iron oxides by carbon

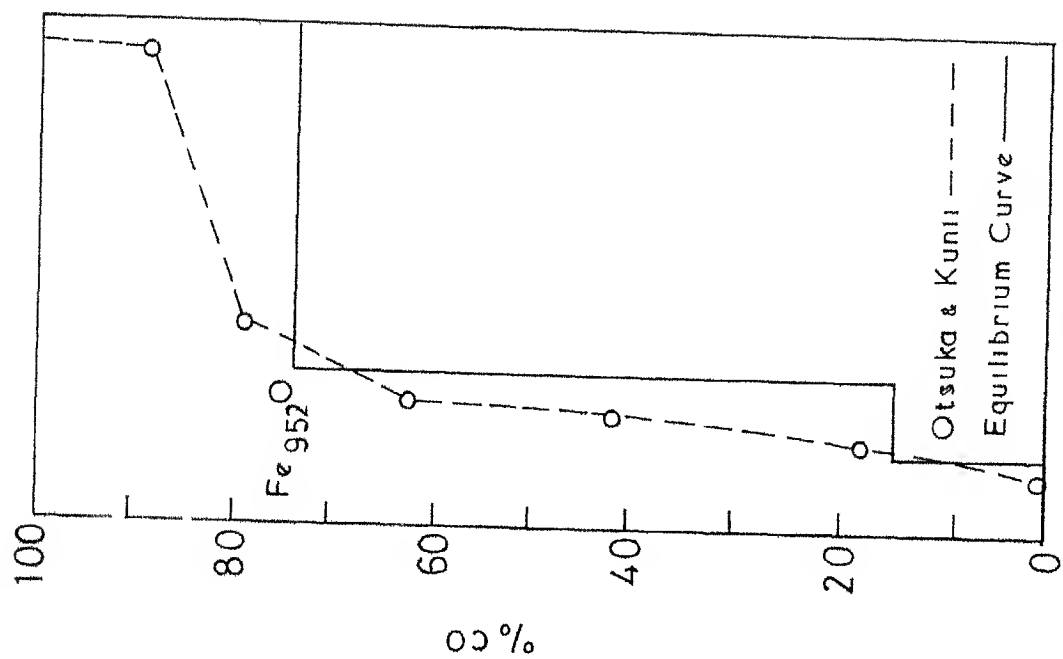
Amongst the investigations on reaction of iron oxide with carbon, only Otsuka and Kunii (24) , determined the instantaneous rates of oxygen and carbon loss. They used 99 pct. pure Fe_2O_3 which was prepared by reacting of iron nitrate at 800°C . The porous ferric oxide obtained had a specific gravity of 4.7 graphite employed for the reduction was electrode graphite (99.8%) with specific gravity of 2.2 and 31 pct. of pore volume. Standard test sample of mixture contained 0.8 grams of Fe_2O_3 and 0.2 grams of graphite. It was mixed and packed in silica bucket (void fraction 0.8) which was suspended by a platinum chain.

During the reaction, gaseous products were continuously removed by a nitrogen stream. At suitable intervals gas samples were analysed by gas-chromatograph. Overall reaction rate was calculated from the flow rate of the gas produced from the reacting solids.

They found that the reduction occurred in two stages. First stage was the formation of FeO from Fe_2O_3 and the second stage was reduction of FeO to metallic Fe. They also observed an increase in the reduction rate after approximately 33 pct reduction which corresponds to complete conversion to FeO. Fig. (1-3) presents typical curves. The first stage had a high activation energy (55-75 Kcal/mole). From this it was concluded that the gasification reaction was rate controlling since the latter also has a high activation energy. There were further proofs for this. The rate increased when the particle size of the graphite was less and it was independent of the particle size of Fe_2O_3 .

The increase of rate at the FeO stage could occur only if the carbon solution reaction was accelerated. So it was interpreted that the metallic Fe produced at the surface of the carbon had the catalytic effect on the gasification reaction. This was supported by the low activation energy for the second stage (15-23.5 Kcal/mole.).

The change in the gas composition as reduction proceeded is shown against composition in equilibrium with various oxide mixtures. In fig 1-4 It is evident that the gas was not reducing enough to allow formation of metallic Fe at early stage.



%Reduction

FIG 14

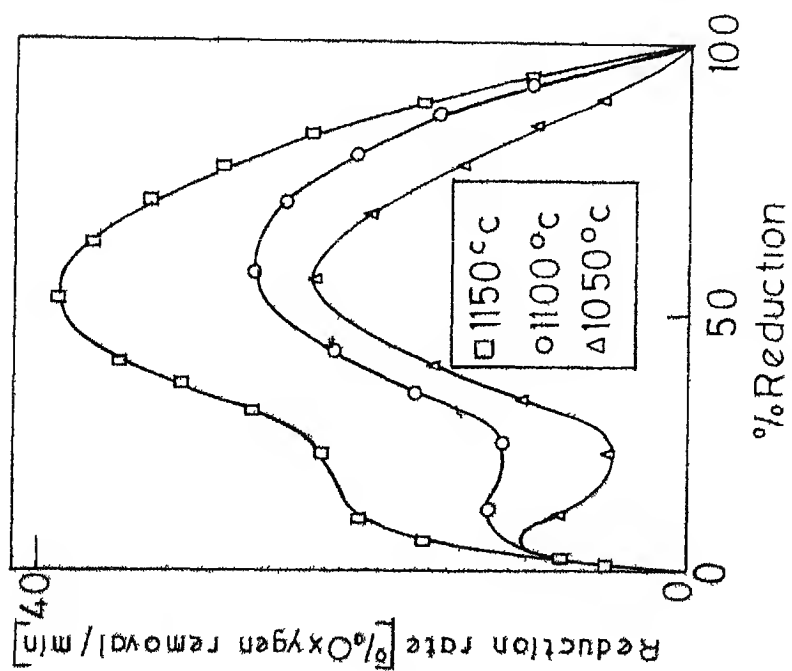


FIG 13

Thus the major conclusions drawn by Otsuka and Kunii were that:

- 1) gasification reaction is the rate controlling and
- 2) reduced iron had catalytic effect on the rate of the reaction.

Besides Otsuka and Kunii, Rao (25) also investigated this reaction and came to the conclusion that gasification reaction is rate controlling.

Since the gasification reaction is chemically controlled, the rate of the reaction is altered by the impurities. This in turn affects the reduction of the iron oxides. Some impurities catalyse the reduction reaction itself.

T.P. Prasad and H.R. Surt (26) have reported that the alkali and alkaline earth salts accelerate the rate of reduction e.g. barium carbonate catalyses the gasification reaction and calcium oxide catalyses the reduction reaction. The accelerating effect of the alkali and the alkaline earth metals was perhaps due to the electronic interaction between the adsorbed oxides of these metals and the oxides being reduced.

While both sodium and potassium carbonates accelerate the reduction, Na_2CO_3 is found to be more effective. This was attributed to the formation of surface active compounds and interaction of sodium ions or atoms.

The rate of reduction also depends on the nature of the carbon used for reduction. The reduction rate was higher with charcoal than with graphite. The activity of carbon also reflects in the degree of reduction.

Certain salts were found to act as retarders. Oxides of Mg, Ti, Al and Si retarded the rate of reduction. The decelerating effect of the aluminium oxide and silica was attributed to the formation of aluminate and silicate.

The study by Otsuka and Kunii is the most comprehensive so far. However their conclusions cannot be held to be generally valid for all the types of materials without corroborating evidence. Also they took too little quantity of graphite. So chances are that the graphite got exhausted before the completion of reduction.

C) Plan of the work:

The following things were decided upon.

- 1) To complete the fabrication of oxygen sensor which was initiated by A.K. Sengupta; alongwith the gas train to purify the gases which will be fed to the oxygen sensor for testing purposes.
- 2) To test its performance using nitrogen oxygen mixtures at various temperatures and concentrations of the oxygen in the mixture.
- 3) To fabricate the reaction cell for the reduction of iron ore from Rajhara mines, Durg, by graphite.
- 4) To arrange for the measurements of instantaneous rates of reduction (rate of oxygen removal from ore) and rate of gasification (rate of carbon loss from graphite). It was planned to accomplish this in the following way.

Precision capillary flow-meters were planned to use in order to know the flow rate of CO-CO_2 gas mixture generated because

of the reaction of iron Ore and graphite. The oxygen sensor then could measure the oxygen potential of the gas which in turn would give the CO/CO_2 ratio as discussed in section (B-1-1). Once the flow rate of gases and the CO/CO_2 ratio is known the rates of evaluation of CO and CO_2 individually and hence the instantaneous rates of the carbon and the oxygen removal can be calculated. To obtain the cumulative loss of carbon and oxygen, numerical integration was thought of.

5. Correlation and interpretation of the data obtained.

CHAPTER II

ApparatusA) Oxygen Sensor:

$ZrO_2 + 10$ mole pct. CaO in the form of a tube was used as the solid electrolyte with following dimensions (0.95 cm I.D. x 1.27 O.D. x 45.5 cms long). It had closed, flat end. It was supplied by Zirconium Corporation of America. It was checked for leaks under vacuum and was confirmed to be vacuum tight. The closed end was platinised inside as well as outside by applying two successive coatings of the platinum paste and heating it to around $900^\circ C$.

The fig 2-1 shows the details of the oxygen sensor and in fig 2-2 combined assembly of the oxygen sensor and the gas-train is shown.

Quartz tube of ¹⁵mm I.D. was used as an enclosure to the S.E. tube with a constriction at the middle, against which the S.E. Tube rested. The other part of the quartz tube was used as preheating chamber. A pt/ pt-10% Rh thermocouple was inserted through the preheating chamber, the tip of which was in contact with the S.E. tube. The pt/10% Rh wire of the thermocouple itself was used as one of the lead wires. To improve the contact a small piece of a pt-wire joined to the thermocouple bead was coiled and kept in between the quartz constriction and the S.E. tube which pressed against the former.

A two hole alumina rod (.635 cm. O.D.) was used inside the S.E. tube to hold the pt-10% Rh lead wire and to transport the reference gas into the cell. The tip of this wire was also coiled to

improve the contact. Tygon tubing was used for all the joints.

To further improve the contact between the lead wires and the -S.E. tube, springs were used, which were supported by the hooks on the quartz tube one end and the brass head fitted on the alumina rod at the other.

To eliminate electrical interference from the furnace windings and to avoid the pick up of other stray emfs a grounded inconel tube surrounding the quartz tube, was inserted into the furnace.

The design is similar to that of Hsueh and Flengas (27) with some modifications. Speciality of this design is that the linear velocity of gas at the constriction can be made high.

The furnace employed for the heating of the S.E. cell was a horizontal tube furnace, which could attain a maximum temperature of about 1100°C . Magnesia asbestos powder along with hot face insulating bricks were used for insulation purposes.

Specifications of the furnace were: =

Maximum power rating = 1.5 Kw.

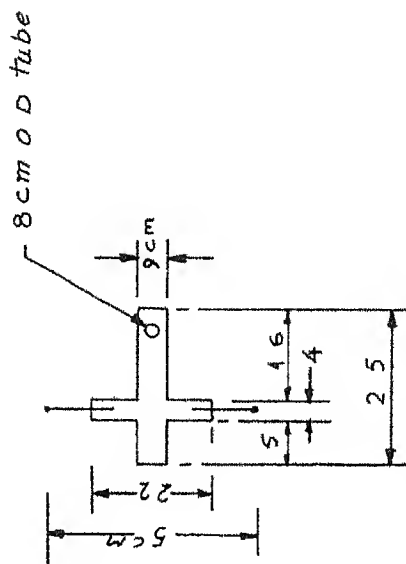
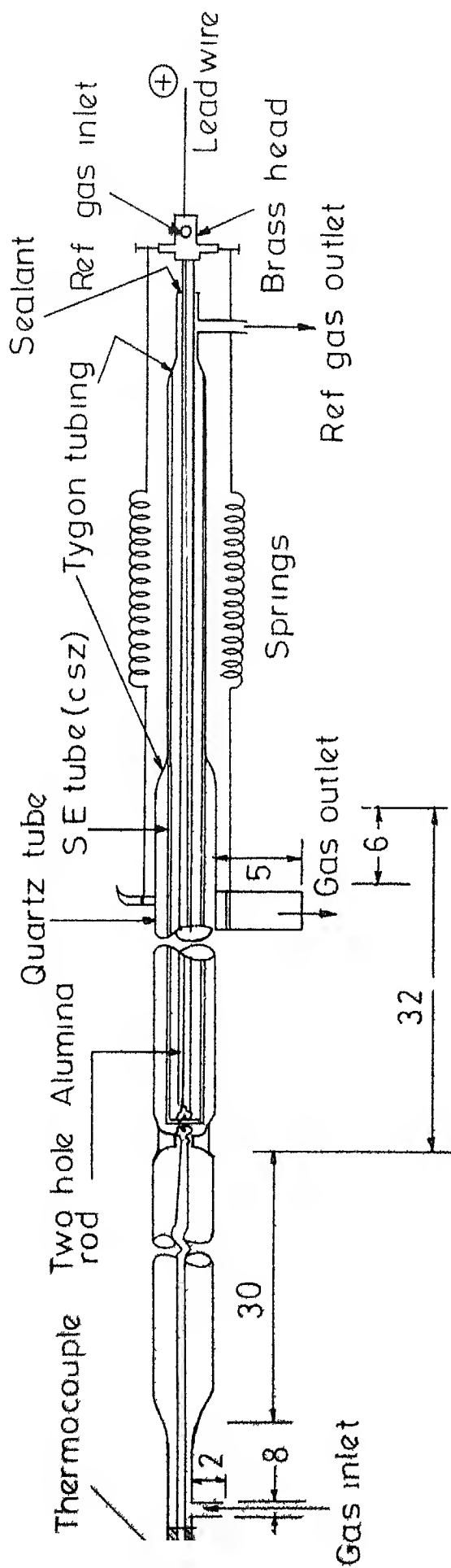
Length of the furnace = 45.7 cm

Outside diameter = 29.2 cm.

Heating element - Kanthal resistance wire

(BSW 16) having a resistivity of $0.01115 \Omega\text{-cm}$

The furnace was fixed on a slotted angle frame work with castor wheels to make it portable. It could be moved vertically to adjust position. Electrical points were fitted on the trolley itself.



Brass head details

SE Tube(csz) — 0.95cm ID x 1 27cm OD
x 45 5cm long

dimensions are in cm

FIG 2 1

The lower portion of the trolley was used to keep vari-
ace, microvoltmeter for emf measurement and also for the gas train
which was employed to purify the gas before passing it through the
solid electrolyte assembly.

Cold junction arrangement for the thermocouple was as
follows. The two ends of the compensating lead wires coming from the
thermocouple were dipped into two small mercury pools which were kept
immersed in water in a Dewar flask. A thermometer was used to mea-
sure the temp of the water.

For measurement of the emf developed, phillips micro-
voltmeter with the following specifications was employed. D.C.
Microvoltmeter pp 9004.

Ranges: 1M Ω input impedance - 0.1 mV - 10V

100m Ω input impedance - 10mV-1000V

Temperature was adjusted manually by a valve.

B) Ore-Carbon reaction assembly:

B-1) Since the amount of gas generated from the reaction of the
iron ore and graphite was expected to be small, the minimum possible
dead volume was aimed at in designing the reaction assembly Fig.
(2-3) shows this.

An 18 mm I.D. and 22 mm. O.D. translucent quartz tube
of 30 cm. length (tube 1) was employed as the reaction tube. To this
a 6 mm I.D. translucent quartz tube was connected at one end.
Through the latter tube a pt/pt-10%Rh thermocouple was inserted,
insulated by a 0.15 cm single bore alumina sheath. The 6 mm silica

tube was also employed as an inlet for the purging gas which was passed over the sample during the pre-heating period. Cold junction arrangements were made for the thermocouple as in the previous case.

A 17.3 mm O.D. silica tube (tube 2) had both the ends closed except for a 5 mm I.D. (tube 3) silica tube concentrically joined to it. It had a quartz hook at one end to which a ring made out of kanthal heating element wire was tied. A quartz crucible with the sample (ore and carbon) was fitted in this ring. Thus the 17.3 mm tube helped in inserting the crucible as well as for taking it out. The inner 5 mm dia tube served as the outlet for the gases.

To seal the gap between tube no. 1 and 2, a water cooled brass coupling was employed. The coupling also facilitated the axial movement of tube 2 in tube 1 without letting any air in. A globar furnace was used for heating purpose.

The out let of tube 3 was connected to a capillary with a simple liquid (di butyl phthalate) manometer in between with the help of a 3 mm, I.D. tube. After the capillary again, a 3 mm I.D. tube led was used to lead the gas to the oxygen sensor. Arrangements were made to mix this gas with an inert gas just before it entered the oxygen sensor. Thus the gas mixture generated in the reaction cell flushed out fast through the oxygen sensor so as to allow in measurement of instantaneous gas composition. This ensured correct CO/CO_2 ratio measurement at a particular time to a considerable extent.

The capillary along with the manometer served as a capillary flowmeter. A set of capillaries was used to cover the desired ranges of flow.

The oxygen sensor and the reaction assembly were kept as close as possible in order to minimize the length of the connecting tube so as to cut down the volume.

CHAPTER III

EXPERIMENTAL PROCEDURES AND MATERIALSA) Procedure for testing of the oxygen sensor:

Inert gas oxygen mixture (N_2+O_2) was employed for testing. The gas train employed for purification of these gases consisted of the flow meters, H.T.S. catalyst (obtained from BASF, Germany) furnace for oxygen removal, gas mixers to mix the gases before feeding it to the cell and U-tubes containing anhydrous $CaCl_2$ and anhydrous to remove the moisture. A bubbler was also used to bypass the gas. The gas mixers consisted of a glass column filled with glass-beads.

Temperature of the solid electrolyte cell, percentage oxygen in the mixture and the flowrate of the gas were the variables. The flowmeters on the N_2 and O_2 lines were calibrated for the respective gases.

The flowmeter reading for both the gases were noted from which the oxygen contents in the mixtures were calculated. The system was allowed to attain steady state after which the steady emf, shown by the microvoltmeter was noted. Temperature was also measured. The microvoltmeter was calibrated with the help of the potentiometer for the necessary correction to the measured emf. When the corrected emf. and the cell temperature were known, corresponding PO_2 could be calculated by using equation (1-1).

The pct. oxygen obtained from flow-meter readings and from the measurement with oxygen sensor were compared in order

to examine the precession of the sensor.

Sometimes air was used as the sample gas. In all the measurements pure O_2 was the reference gas.

Sometimes the sensor chamber was evacuated when switching from one composition to the other, especially at low flow rates of N_2 and O_2 .

Attempts were also made to analyse the gas by gas chromatograph. In these cases the three values of pct. oxygen obtained from 1) gas chromatograph 2) flow-meters and 3) oxygen sensor were compared.

B) Reduction of iron-ore with graphite:

Iron ore of Rajhara mines (Durg) was chosen for these experiments. It had the following analysis: Fe- 66.1%, SiO_2 1.64%, Al_2O_3 3.8%, TiO_2 absent. Fe^{+2} ions could not be traced. From this the oxygen content of the ore was estimated to be 28.3 wt. pct, which matched with the oxygen content calculated from weight loss by hydrogen reduction. The ore was found to contain 3.6 pct. moisture. This moisture was chemically held and could be removed only by heating to a higher temperature for at least 5 minutes. The imported low ash electrode graphite supplied by Navinchandra and company was used for the experiments. Total ash content was estimated to be 1.12 per cent. The size of the graphite chosen was -200 mesh. Experiments were conducted at temperatures of approximately $935^\circ C$, $975^\circ C$, $1015^\circ C$ and $1050^\circ C$. Two sizes of the iron ore were chosen: 1) -325 mesh powder 11) 5 mm diameter pellets.

B-2 Preparation of pellets

The ore was mixed with appropriate amount of water. Green pellets were made by hand-rolling. They were dried in an oven at about 100°C for sometime and then fired to 900°C for about $2\frac{1}{2}$ hours. The dried iron ore powder, graphite and pellets were stored in a desiccator.

B-3 Preparation of the sample

For the experiments approximately one gm. iron ore was mixed with 0.4 gm graphite powder and then filled in the quartz crucible with intermittent hand-ramming. The crucible was weighed with and without the sample to know the initial weight of the sample. Then the crucible was fitted in the kanthal ring of tube 2 and inserted halfway in the heated reaction tube for preheating. During preheating an inert gas was made to flow over the sample to remove the moisture etc. Preheating was done for around five minutes. Then the flow of the inert gas was diverted to the oxygen sensor and the sample was pushed to the reaction zone. This time was noted down as the zero time for the reaction. After this at suitable intervals flow-meter readings and S.E. cell emf. were noted down. Emfs were measured by philips V.T.V. M. (Phillips GM 43798, S/N 1098 range-1mV-1000V) The reaction temperature and cell temperature were measured intermittently. V.T.V.M. was calibrated from time to time by potentiometer. The flow of the inert gas purging the oxygen sensor was kept at around 120-130 cc/min. When the reduction was nearly complete the reaction was stopped by taking out the sample. It was then weighed in order to know the weight loss.

In some cases the N_2 flow caused some static pressure in the gas line from the reaction chamber by which some positive

TABLE 3-1
Calibration of capillaries by argon at 30°C

Capillary No.	$Q V_g \Delta h$ Correlation	$Q V_g \Delta h$ correlation after zero correction
1	$Q = 9.8339 \Delta h + 0.0669$	$Q = 9.83 \Delta h$
2	$Q = 3.7522 \Delta h + 0.1939$	$Q = 3.80 \Delta h$
3	$Q = 0.5807 \Delta h - 0.3974$	$Q = 0.5583 \Delta h$
4	$Q = 0.1542 \Delta h - 0.1106$	$Q = 0.15 \Delta h$

CHAPTER IV

RESULTS AND DISCUSSIONS ON PERFORMANCE OF OXYGEN SENSOR

As mentioned in chapter 3, the first part of this investigation consisted of testing the performance of the oxygen sensor. This was done by mixtures of O_2 and N_2 . The oxygen content of this gas mixture was calculated from flow-meter readings and then compared with the oxygen sensor data. This was done at several oxygen contents and temperatures. Table 4-1, and fig. 4-1 present the data. In table 4-1, while calculating the percentage error in the measurement of oxygen concentration by the oxygen sensor, the values of oxygen concentration obtained from the flowmeter readings were assumed to be the correct ones.

These are the 50 pct readings in which the pct. error was below 20 pct. The remaining readings were rejected since the pct errors were more than 20 pct in those cases. Figs 4-1 and 4-2 show the pct error at various gas compositions and temperatures.

The possible sources of errors are:

1) Improper electrode contact

If the lead wires have the improper contact with the platinized surface of the solid electrolyte tube, the emf measured will be less than the actual one and as the calculated value of pct O_2 will turn out to be higher. In some cases, application of the pressure by hand showed increase in the emf reading as more number of springs were employed to improve the contact.

2) Electronic conduction in the solid electrolyte tube:

If this is present, then also the emf measured will be

Table 4-1

Performance of oxygen sensor

Sr. No.	O ₂	Flow rates ccs/min	Cell Temp °K	Cell Emf mV	pot. O ₂ from emf	pot O ₂ from flow meters	pot error
1		Air	1086	35.4	21.47	20.9882	+ 2.50
2		air	1086	35.5	21.93	20.9882	+ 4.49
3		air	1115	35.73	22.53	20.9882	+ 7.35
4		air	1121	36.5	22.06	20.9882	+ 5.11
5		air	1177	38.2	22.17	20.9882	+ 5.63
6.		air	1180	37.1	23.24	20.9882	+ 10.73
7.		air	1191	39.7	21.28	20.9882	+ 1.39
8.	24.95	680	1026	72.4	3.61	3.536	+ 7.65
9.	7.95	1136	1050	108.5	0.76	0.6952	+ 9.59
10.	6.5	124	1059	68.0	4.795	4.981	- 3.77
11.	6.5	234	1041	79.1	2.954	2.705	+ 9.55
12.	9.0	142	1041	62.1	6.272	5.96	+ 5.24
13.	8.57	81	1041	50.3	10.61	9.569	+ 10.68
14.	5.679	514.0	1045	96.0	1.595	1.153	+ 20.47
15.	30.57	650.0	1090	71.8	4.701	4.255	+ 11.0

16.	6.1423	99.5	1103	65.71	6.236	6.456	- 2.43
17.	5.071	129.	1114	76.5	4.121	3.782	+ 8.96
18.	5.071	204.	1115	85.3	2.869	2.425	+13.31
19.	5.6423	104.	1152	72.4	5.384	5.157	+ 4.61
20.	5.6423	147.5	1153	79.75	4.053	3.685	+ 9.44
21.	0.957	700.	1177	157.	0.1573	0.1209	+ 14.03
22.	7.86	56.	1179	53.2	12.3	11.93	+ 3.10
23.	6.5	139	1181	76.2	4.998	4.498	+11.12
24.	5.071	311.	1182	126.2	0.9551	0.9776	- 2.22
25.	16.57	390.	1182	76.0	5.259	4.659	+12.86
26.	7.6423	111.0	1184	70.0	6.45	6.442	-0.10
27.	7.6423	274.3	1185	90.7	2.864	2.709	+5.72
28.	6.5	257.5	1186	91.5	2.784	2.4321	+13.07
29.	2.786	279.0	1186	115.4	1.083	0.9857	+9.54
30.	9.0	575	1248	114.5	1.801	1.542	+16.8

2 for air pot. O₂ was calculated assuming 50 pot humidity at 760 mm Hg and 25°C.

Calibration for air at various temperatures

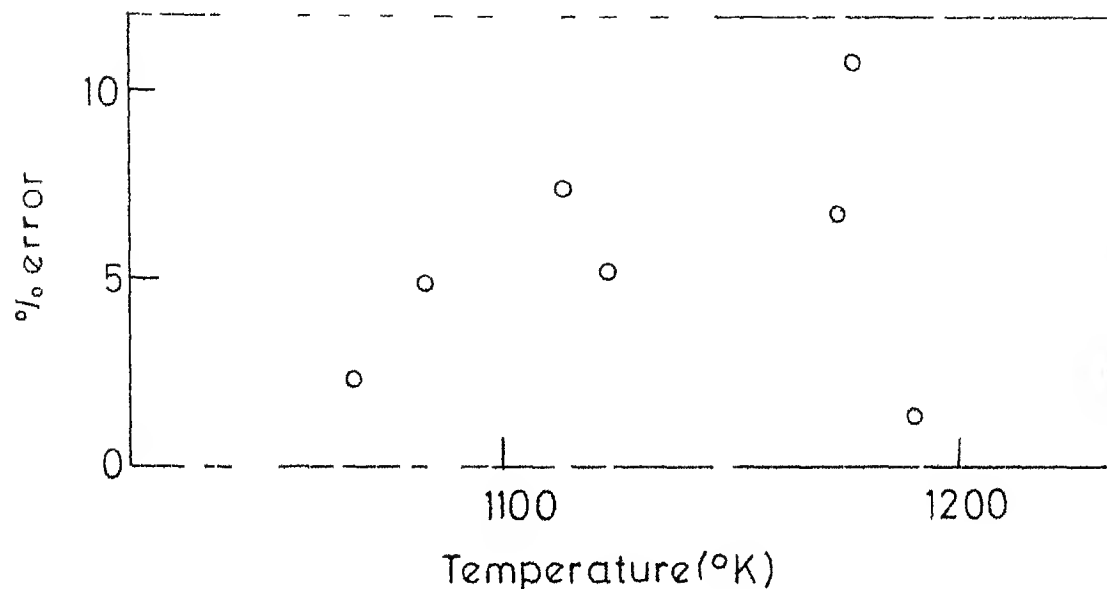


FIG 4-1

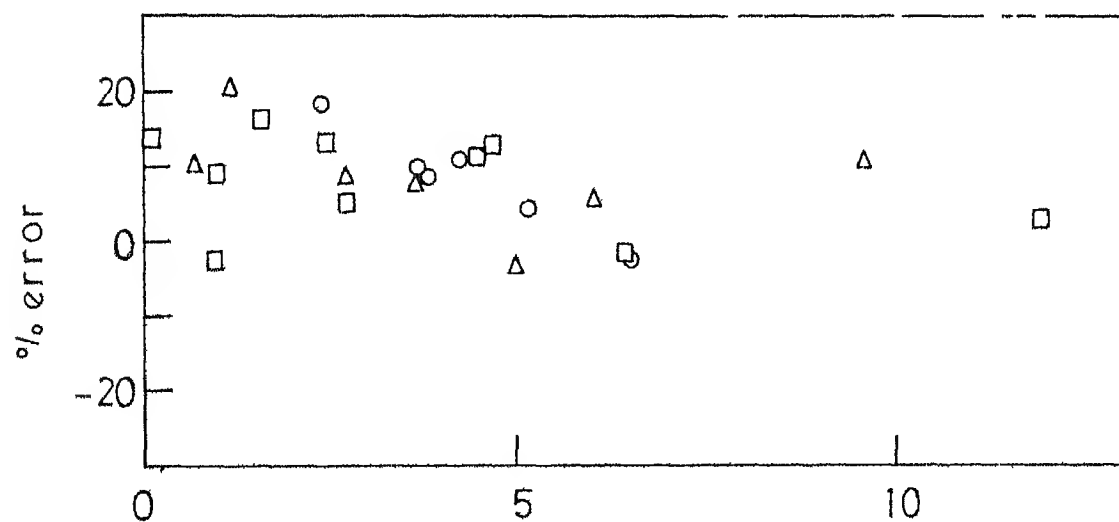


FIG 4-2

%Oxygen in the gas mix

Temperature range °K

△ 1000 1050

○ 1050 1150

□ 1150 on wards

less than the actual. Since the flow rate were quite appreciable this source of error is not expected.

3) Scatter in the flowmeter readings:

If the actual amount of gas going into the system is different from that of the value calculated from the flowmeter calibration curve, error will be introduced in the calculation of oxygen concentration. Also the error in the measurement of Δh will introduce error in calculating oxygen concentration. Flowmeter calibrations were repeated in order to minimize this source of error.

4) Error in temperature measurement:

The thermocouple used was calibrated with the standard reference thermocouple and was found to be reading the correct temperature. So this error can be assumed to be absent.

5) Insufficient pre-heating of the flowing gas:

If the gas velocity is too high, it may not get heated to the cell temperature properly. So the system will not be in equilibrium which is assumed to be so in further calculations. Also it may cool down the outer portion of the solid electrolyte tube, causing the temperature gradient ^{the} in/ tube itself. So the measurements made will be erroneous. However at low flow rates also errors were present

6) Leak in the gas train or apparatus:

If there is any leak after the flow meter in the pure gas line, the actual gas getting mixed will be different from what is being measured which will cause the error in oxygen concentration. Also if the air is leaking in, it will also change the oxygen concentration. To get ~~rid of this sort of error~~ attempts were

made to make it leak proof. Still tiny leaks were present which could not be detected. However the leakage rate was hardly 2-3 cc/min and it was outwardly. Therefore it is not expected to affect the readings.

7) Errors in potentiometers and microvoltmeter measurements of emf:

Errors in microvoltmeter readings were minimized by point to point calibration with potentiometer all the time.

To summarize, the improper electrode contact and the scatter of the flow meters especially at low oxygen may be the major sources of error.

Since the oxygen sensor was to be used to measure the CO/CO_2 ratio of the gases produced from the reaction of iron ore and graphite, doubt arose about the accuracy of the ratio measurement and of the further calculations of the rate of oxygen and carbon weight loss. For this, sample calculations were made to estimate the pct. error involved in oxygen loss rate (\dot{W}_O) as a consequence of error in oxygen sensor measurement. Table 4-2 shows the results of these calculations.

Let the error in P_{O_2} measurement by oxygen sensor be 30 pct.

$$\text{Since } \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \propto \sqrt{P_{O_2}} \quad \text{error in } \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \quad \text{is 15 pct.}$$

Thus it may be noted that from table 4-2 the errors in the rate of oxygen and carbon loss would be small. Gas composition also would not be in error seriously.

So it was decided to proceed with the study on reduction of iron ore by carbon.

Table 4-2

Estimation of errors in oxygen loss rate

pet. CO ₂ in co-CO ₂ mixture	Theoretical CO ₂ /CO ratio	Measured CO ₂ /CO after + 25 pet error	Measured gas comp. pet. CO ₂	Error in H ₂ , pet.
10	1/9 = 0.11	0.127	11.2	+ 1.0
50	1/1 = 1	1.15	53.5	+ 2.2
90	9/1 = 9	10.35	91.2	+ 0.7

(H₂ ∝ (Rate of flow of CO + 2 × rate of flow of CO₂)

CHAPTER V

Results of Iron-Ore-Graphite Reactions

Raw data consisted of the reaction temperature, weight of the sample mixture of iron ore and graphite, Δh readings of the capillary flow meter at suitable time intervals and corresponding emf (E) of the oxygen sensor. However the values of E and Δh are hardly useful as such. Hence these were fed to the computer for the following calculations.

A) Calculation of CO/CO_2 ratio:

As mentioned before, equilibrium may be assumed to prevail for the following reaction in the oxygen sensor.



$$\therefore 2 \Delta G^\circ_{CO_2} - 2 \Delta G^\circ_{CO} = \Delta G^\circ \dots (5.2)$$

For the reaction (5.1) equilibrium constant K is equal to

$$\left[\frac{P_{CO_2}}{P_{CO}} \right]^2 \times \frac{1}{P_{O_2}} \dots (5.3)$$

$$G^\circ = -RT \ln K \dots (5.4)$$

where T = Oxygen sensor temperature, $^\circ K$.

$$\begin{aligned} \therefore G^\circ &= -RT \ln \left[\left(\frac{P_{CO_2}}{P_{CO}} \right)^2 \times \frac{1}{P_{O_2}} \right] \\ &= -4.606 T (2 \log \frac{P_{CO_2}}{P_{CO}} - \log P_{O_2}) \dots (5.5) \end{aligned}$$

Since the reference gas in the oxygen sensor had approximately 0.96 fraction of oxygen:

$$\log \frac{0.96}{P_{O_2}} = 20.139 - \frac{E}{T} \dots\dots\dots (5.6)$$

(from equation (11))

$$\therefore \Delta G^\circ = 4.606T \left[-0.02 - 20.139 \frac{E}{T} \right] - 9.212T \log \frac{P_{CO_2}}{P_{CO}} \quad (5-7)$$

Table 3-1 shows the values of ΔG° at various temperatures. For the temperatures between 1100°-1200°K by interpolation:

$$\Delta G^\circ = -85,020 + 41.4 (T - 1200) \text{ Gals/mole} \dots (5.8)$$

Thus once the oxygen sensor temperature and the cell emf (E) are known from equations (5-7) and (5-8), the CO/CO₂ ratio, which is the only unknown, can be determined.

B) Correction for the capillary constant:

The calibration of the capillary was done with the help of argon gas. But since the gas flowing through the capillary during the reaction was a CO-CO₂ mixture instead of argon, the corresponding viscosity corrections had to be made. Viscosity of the mixture is a function of the individual mole fractions.

$$\mu_{mix} = \sum_{i=1}^2 \frac{x_i \mu_i}{\sum_{j=1}^2 x_j \phi_{ij}} \quad (5-9)$$

$$\text{where } \phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{\mu_i}{\mu_j} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_i}{M_j} \right)^{1/4} \right]^2 \quad (5-10)$$

M stands for the molecular weight and

μ stands for viscosities

on simplification for mixture of CO and CO it gives

TABLE 5-1

Values of ΔG° at various temperatures.

Temp. °K	ΔG°_{CO} cal/mole	$\Delta G^\circ_{CO_2}$ cal/mole	ΔG° cal/mole
1000	- 47,940	- 94,610	- 94,340
1100	- 50,080	- 94,640	- 89,180
1200	- 52,180	- 94,660	- 85,020
1300	- 54,240	- 94,680	- 80,880
1400	- 56,310	- 94,690	- 76,750

$$\mu_{\text{mix}} = \gamma_1 + \gamma_2 \quad \dots \quad (5-11)$$

$$\text{where } \gamma_1 = \frac{1.582 \times 10^{-4} p_{\text{CO}}}{p_{\text{CO}} + 1.5831 p_{\text{CO}_2}} \quad \dots \quad (5-12)$$

$$\text{and } \gamma_2 = \frac{1.495 \times 10^{-4} p_{\text{CO}_2}}{p_{\text{CO}_2} + 0.89974 p_{\text{CO}}} \quad \dots \quad (5-13)$$

C) Instantaneous rates of generation of CO and CO₂

Once the CO/CO₂ ratio is known and the corresponding viscosity correction made, total flow rate 'Q' can be calculated by using the formula:

$$Q = (\text{capillary constant}) \times \frac{\Delta h}{\mu_{\text{mix}}} \quad \dots \quad (5-14)$$

$$\therefore Q_{\text{CO}} = Q \times \text{CO fraction cc/min.} \quad \dots \quad (5-15)$$

$$\text{and } Q_{\text{CO}_2} = Q \times \text{CO}_2 \text{ fraction cc/min.}$$

D) Calculation of instantaneous rates of loss of carbon and oxygen:

Since 1 mole of CO corresponds to 1 mole of carbon and oxygen each and one mole of CO₂ corresponds to 1 mole of carbon and 2 moles of oxygen.

$$\dot{W}_C = \text{Instantaneous rate of wt. loss of carbon}$$

$$= (Q_{\text{CO}} + Q_{\text{CO}_2}) \times 12 / (22400 \times 60) \quad \dots \quad \text{gms/sec (5-16)}$$

$$\text{and } \dot{W}_O = \text{Instantaneous rate of wt. loss of oxygen}$$

$$= (Q_{\text{CO}} + 2 \times Q_{\text{CO}_2}) \times 16 / (22400 \times 60) \quad \text{gms/sec} \quad \dots \quad (5-17)$$

E) Cumulative loss of 'C' and 'O' and net loss of 'O'

Since the oxygen content of the ore is determined to be 28.3 pct. by weight (30.0 pct. in case of pure Fe_2O_3), by knowing the amount of ore or pure Fe_2O_3 present in the sample, the total weight of the sample fed into the reaction chamber was known.

Trapezoidal rule was employed to numerically integrate instantaneous rates of removal of carbon or oxygen with respect to time. This gave the cumulative wt. loss of carbon and oxygen.

The percentage oxygen removal was obtained from the cumulative oxygen loss (W_L) and the total oxygen content at the beginning of the experiment.

The following things were printed in the output of the computer program:

- 1) Time, min t_i t_{i+1} $\Delta t = t_{i+1} - t_i$
- 2) Oxygen sensor emf (E), volts
- 3) Instantaneous rate of 'O' wt. loss (\dot{W}_O), gms/sec.
- 4) Cumulative oxygen weight loss (W_L), gms
- 5) pct. oxygen loss
- 6) Instantaneous rates of 'C' wt. loss (\dot{W}_C) gms/sec.

The sum of the cumulative weight losses of oxygen and carbon at the end should match with the experimentally determined total weight loss (W_{TG}) if the experimental errors are low.

Table 3-2 shows the experimental conditions of the various experiments performed with different materials.

Appendix- I presents the computer program.

Appendix- II gives a few sample computer printouts.

Table A-2

Experimental conditions of various experiments

Expt. No.	Material	Reaction temp.	S. E. cell Temp. °C	W_{TG} gms	Total time of experi- ment, min	Capill- ary No.
1	Ore powder +graphite	1047	847	0.5445	23	1
2.	—do—	1042	843	0.5113	23	1
3.	—do—	1013	836	0.5180	37	3
4.	—do—	974	821	0.5753	161	2
5 .	—do—	933	825	0.1752	185	4
6.	Ore pellets +graphite	1054	831	0.5193	73	2
7.	—do—	1052	831	0.3485	46	2
8.	—do—	1019	831	0.4036	56	3
9.	—do—	972	818	0.4034	110	2
10.	pure Fe_2O_3 +graphite	965	823	0.4289	202	4
11.	—do—	938	838	0.3862	254	4

CHAPTER VI

DISCUSSIONS ON RESULTS OF IRON ORE-GRAPHITE REACTION

A) Reliability of the results:

As computer print out attached in Appendix II reveal, there are following problems with the results:

- i) CO content of gas is absurdly low (0-0.15)
- ii) Percent reductions are exceeding 100 in many cases. This is not possible.
- iii) In some experiments, notably those with pellets, gas evolution was appreciable even when the pct. reduction was close to 100 percent.

Computer calculations were also carried out assuming that the oxygen partial pressure as monitored by the sensor corresponded to the CO-CO₂-O₂ equilibrium at the reaction temperature. Some of these calculations are presented in Appendix III. As may be noted, the CO-content of the gas varies between 0-0 pct, which is reasonable.

From this it was concluded that the equilibrium $\text{CO(g)} + 1/2 \text{O}_2\text{(g)} = \text{CO}_2\text{(g)} \dots\dots (3-1)$ remained essentially 'frozen' even when the gas was being passed through the oxygen sensor. This could be due to comparatively lower temperature in the oxygen sensor and perhaps the slowness of the above reaction.

Therefore further consideration of the data were based upon the latter calculations; since it gave reasonable values of the gas composition. However, it was decided to ignore the gas composition data altogether. Rate of carbon gasification (\dot{W}_C) is independent of the gas composition since one mole of CO as well as one mole of CO₂ contains one mole of carbon. So the \dot{W}_C can be obtained just by knowing the flow

rate of the gas and the gas composition is not required at all. Therefore, rate of gasification was used as a measure of the rate of reduction, for interpretation of data.

Tunkdogan and co-workers (28) have shown that rate of gasification is proportional to the weight of carbon. Therefore fractional rate of carbon gasification was preferred.

$$\text{Fractional } w'_c (h_{e,f}) = \frac{w_s}{\text{Original wt. of carbon in the mixture}} \quad \dots(6.1)$$

The data, as processed by assuming 'frozen' $\text{CO}-\text{O}_2$ equilibrium were assessed on the basis of the following considerations.

- i) Is the qualitative nature of the variation of gas composition with pct reduction reasonable (as in fig. 1-4) ?
- ii) Is the final pct reduction less than 100 percent ?
- iii) Does the total weight loss as arrived by integration using Trapezoidal rule match with the experimental weight loss measurement (W_{TG}) ?
- iv) Was the reaction continuing appreciably even when the pct reduction was more than 100 pct ?.

Table 6-1 summarizes some of these informations.

The experiments where experimental weight loss data were not available were rejected alongwith few others which were grossly irregular. The rest have been included in table 6-1. The experiments have been classified as good, satisfactory and poor.

An experiment considered good had the following characteristics

- i) The qualitative nature of variation of gas composition with pct. reduction was reasonable.

TABLE 6.1

Calculations on the basis of iron CO-CO_2 - O_2 equilibrium

Expt. No.	Materials	Reaction temp. °C.	Pct O loss	Total (O+C) loss calculated gms	$\frac{W}{T}$ gms	Remark on data	Basis of correction
1	ore powder + graphite	1047	132.7	0.7714	0.3445	S	100 pct reduction
2.	--do--	1042	163.0	0.4391	0.5113	S	----- do -----
3.	--do----	1013	90.3	0.5180	0.4036	G	----- do -----
4.	--do----	974	194.5	0.8323	0.5753	S	y = 3/1
5.	--do----	933	23.2	0.0894	0.1762	F	y = 1/1
6.	Ore pellets + graphite	1024	131.9	0.6294	0.5193	G	100 pct reduction
7.	--do--	1032	81.1	0.3836	0.3485	G	y = 3/1
8.	--do----	1019	84.1	0.3687	0.4035	G	y = 2/1
9.	--do----	972	131.0	0.5264	0.4934	S	y = 2/1
10.	Pure Fe_2O_3	935	128.5	0.4196	0.4289	G	100 pct reduction
1) d/f	graphite + graphite	938	126.1	0.3779	0.3862	G	----- do -----

S - Satisfactory

G - Good

F - Poor.

- ii) Final pct. reduction was not too different from 100 pct.
- iii) Calculated and experimental weight loss matched reasonably.
- iv) The reaction more or less had subsided towards the end.

B0 Corrections to processed data:

The above assessment pointed out that one of the likely sources of error was in the flow rate measurement at high flow-rates. In this case the gas perhaps did not cool to room temperature while passing through the flow meter causing the error in the flow measurement. Also erroneous gas composition would lead to erroneous viscosity values.

Based on all these assessments, it was felt that the final results should be corrected on the basis of the following assumptions.

- i) Experimental total weight loss (W_{TE}) is correct.
- ii) A reasonable CO-content of the gas can be guessed.
- iii) Pct reduction cannot exceed 100 pct.

Since causes and natures of errors etc. as assessed were not the same for all experiments, procedures for correction differed from experiment to experiment. However, they fall into the following two broad categories.

- 1) For the experiments where the reaction had subsided, the last pct. reduction should correspond to 100 pct. appreciably. Hence the basis of correction was to assume that the last reading corresponds to 100 pct reduction.

$$W_G (\text{Corrected}) = W_{TE} - 0.223 \times \text{wt. of ore} \dots (6-2)$$

$$\text{or} \quad (0.3) \quad (\text{wt. of pure } \text{Fe}_2\text{O}_3)$$

$$\dot{W}_G (\text{corrected}) = \frac{\dot{W}_G (\text{corrected})}{W_G (\text{as per original calculation})} \times \dot{W}_G (\text{uncorrected}) \quad (6.3)$$

$$\text{Corrected pct reduction} = \frac{\text{pct. reduction}}{\text{final pct reduction(original)}} \times 100$$

2) For experiments where gas evolution continued appreciably at the end, a certain average CO/CO₂ ratio (1/1, 3/2, 2/1 or 3/1), depending on reaction temperature was assumed as y . Then

$$\text{Since, CO fraction} = \frac{y}{1+y} \quad \text{.....} \quad (6.4 \text{ a})$$

$$\text{and CO}_2 \text{ fraction} = \frac{1}{1+y} \quad \text{.....} \quad (6.4. \text{ b})$$

$$\begin{aligned} \frac{\text{Moles of O lost}}{\text{Moles of C lost}} &= \frac{1/2 \frac{y}{1+y} + \frac{1}{1+y}}{\frac{y}{1+y} + \frac{1}{1+y}} \\ &= \frac{1/2 y + 1}{y + 1} \end{aligned} \quad (6.5)$$

$$\therefore W_O = \frac{32}{12} \times \frac{y+2}{2(y+1)} W_C \quad \text{.....} \quad (6.6)$$

$$\text{Also } W_{TE} = W_O + W_C \quad \text{.....} \quad (6.7)$$

$$\text{Hence, } W_C (\text{corrected}) = W_{TE} / \left(1 + \frac{32}{12} \times \frac{y+2}{2(y+1)}\right) \quad (6.8)$$

$$W_O (\text{corrected}) = W_{TE} - W_C (\text{corrected}) \quad \text{.....} \quad (6.9)$$

\dot{W}_C (corrected) is obtained from equation (6.3)

$$\text{pct. Reduction (corrected)} = \frac{\dot{W}_O (\text{corrected})}{\dot{W}_O (\text{Original})} \times \text{pct reduction(original)} \quad (6-10)$$

If pct reduction (corrected) \simeq 100 the final reading was further normalized to 100 pct; otherwise not.

Appendix - IV presents corrected values of fractional carbon loss rate ($\dot{W}_{C,f}$) and pct. reduction. Figures (6-1) to (6-4) show $\dot{W}_{C,f}$ Vs. pct. reduction curves for various experiments.

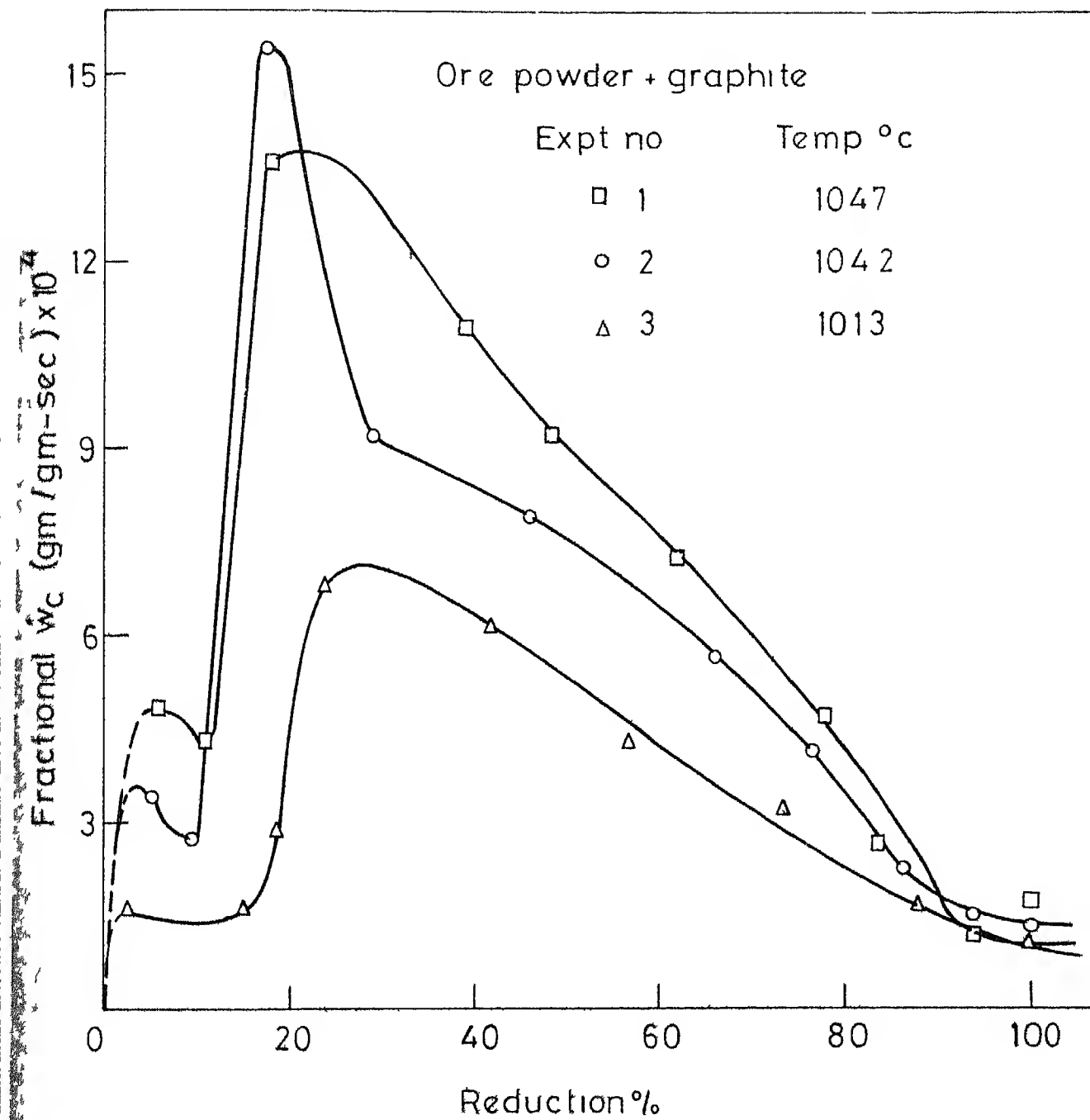


FIG 6-1

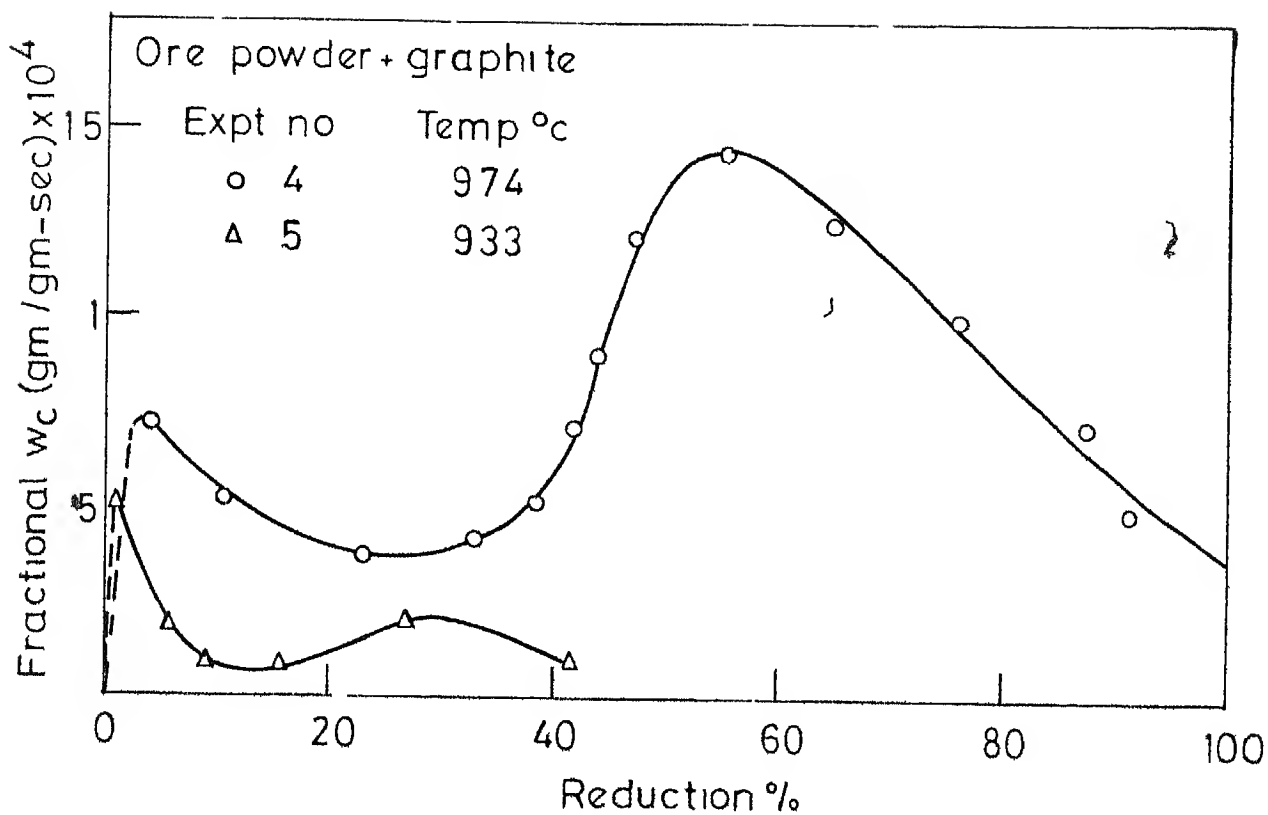


FIG 6-2

1 1 FUR
CENTRAL LIBRARY
10 1 1 4 15 1

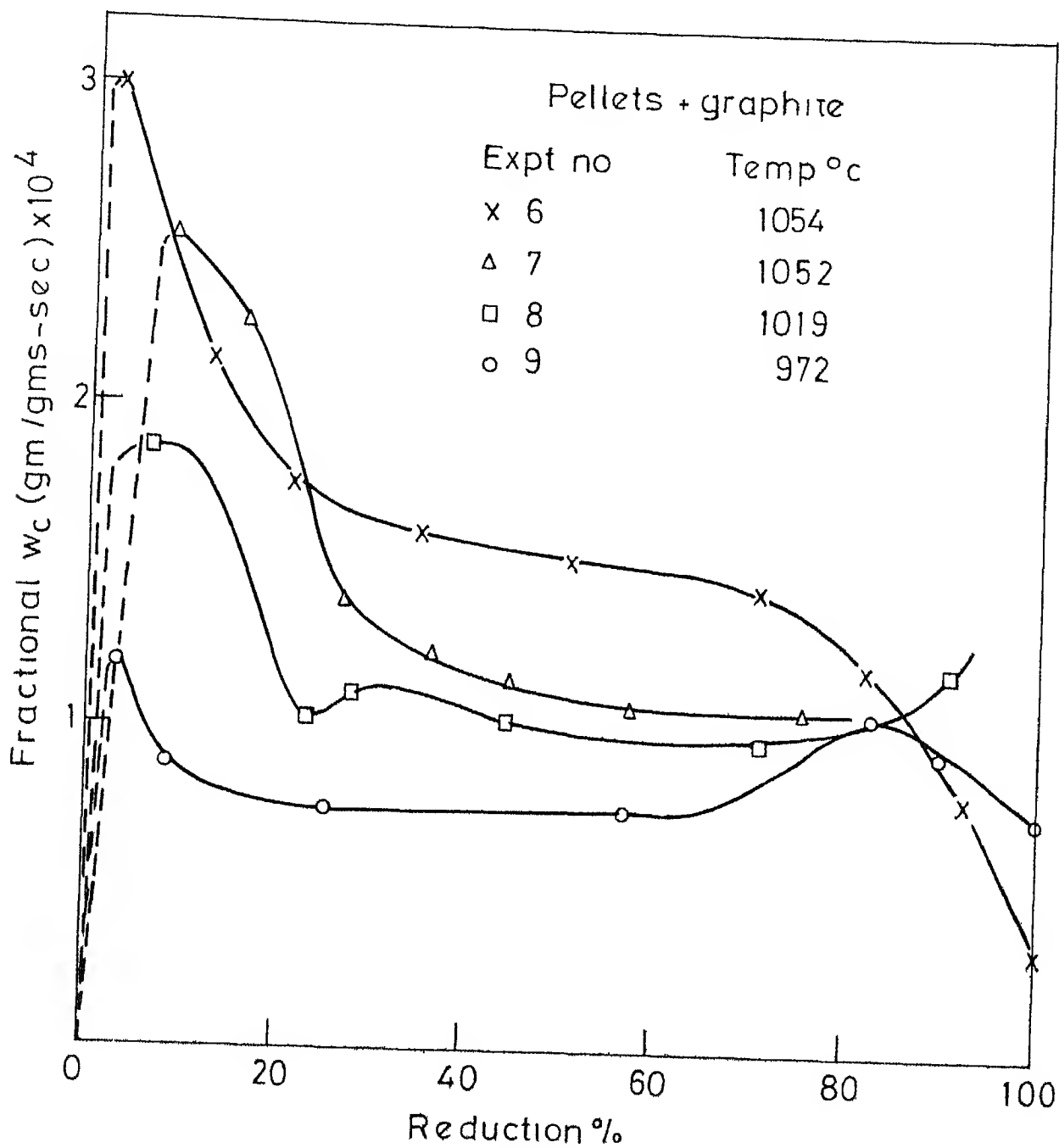


FIG. 6-3

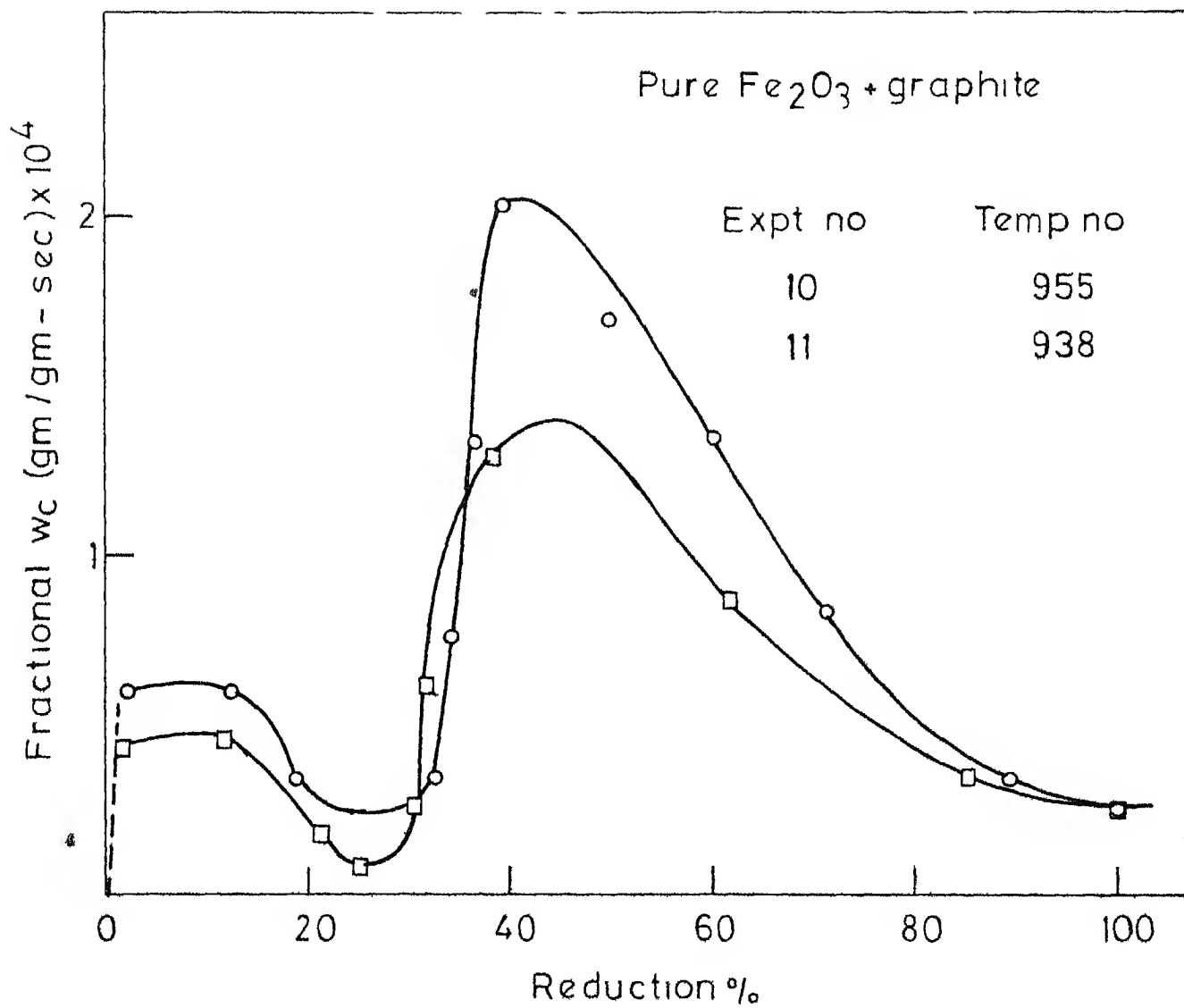
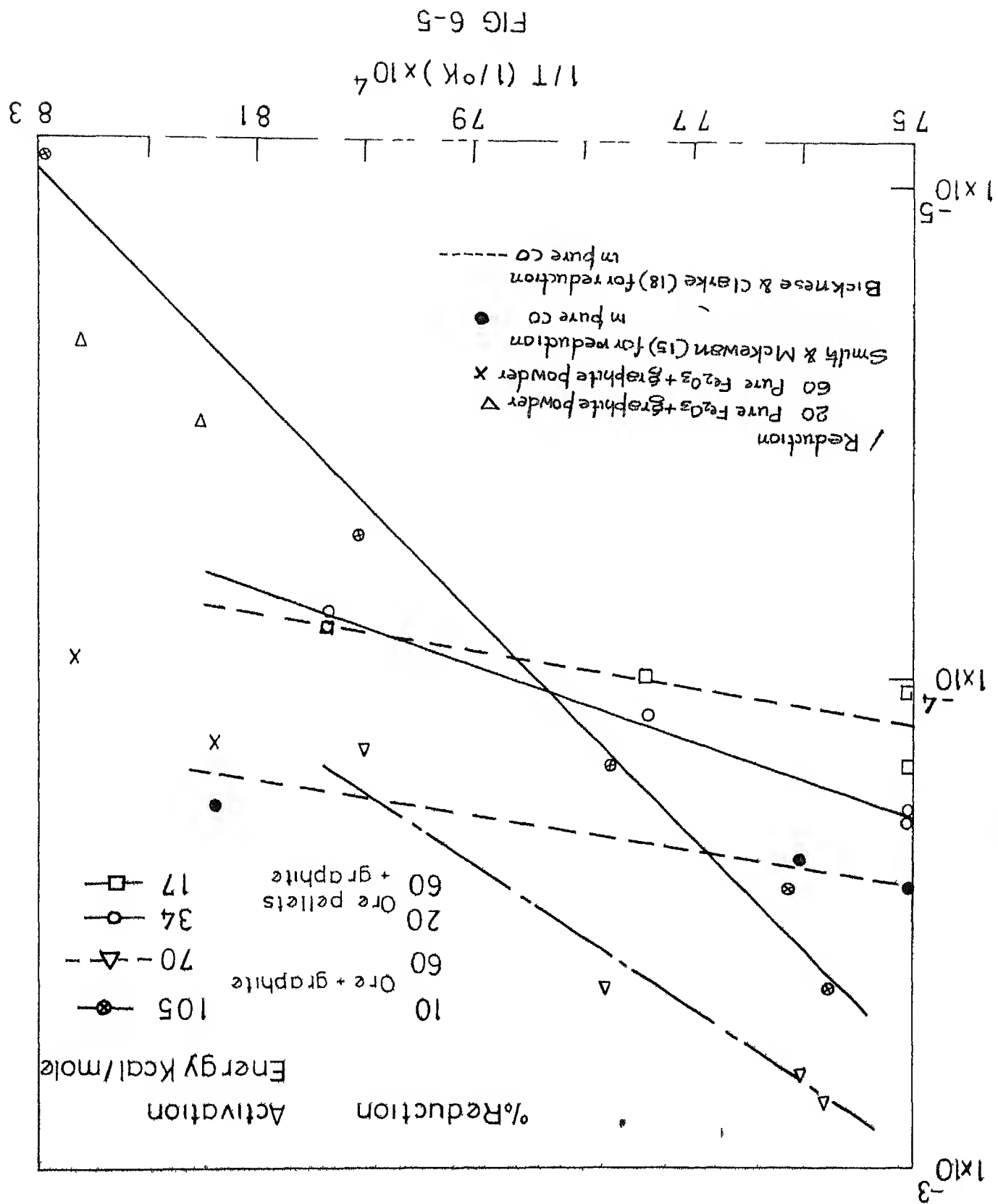


FIG 6-4



APPENDIX - I

COMPUTER PROGRAMME

A P P E N D I X - II

SAMPLE COMPUTER PRINTOUTS ASSUMING

CO-CO₂-O₂ EQUILIBRIUM AT OXYGEN SENS

SOR TEMPERATURE.

EXP RIM NT NO. = 4

REACTION TEMPERATURE = 574 C000

SOLID ELECTROLYTE CELL TEMPERATURE = 82.0 C000

CAPILLARY CONST = C.6608E-C3

WEIGHT OF THE CRF = C.9773

TIME (MINS)	VOLTS	DEL F (GMS)	FRACTION CC	INS.O LOSS (CMS/SEC)	CUM.C LOSS (CMS)	PCT.O LOSS	INS.C LOSS (GMS/SEC)
2.0	0.150	0.00	0.0000	0.1051E-01	0.0139	5.0227	0.3946E-04
4.0	0.150	0.80	0.0000	0.8449E 04	0.0096	0.0000	0.3157E-04
5.0	0.155	0.80	0.0000	0.8419E 04	0.0046	8.909	0.3157E-04
6.0	0.155	0.70	0.0000	0.7367E-04	0.0294	0.0000	0.2769E-04
9.0	0.150	0.70	0.0000	0.7367E-04	0.0426	5.0000	0.2769E-04
14.0	0.155	0.60	0.0000	0.6314E-01	0.0031	0.0000	0.2368E-04
18.0	0.160	0.60	0.0000	0.6314E-04	0.0783	0.0000	0.2368E-04
20.0	0.160	0.50	0.0000	0.5262E-04	0.0852	0.0000	0.1973E-04
22.0	0.165	0.50	0.0000	0.5262E-04	0.0916	0.0000	0.1973E-04
23.0	0.160	0.50	0.0000	0.5262E-04	0.0947	0.0000	0.1973E-04
27.0	0.165	0.50	0.0000	0.5262E-04	0.0073	0.0000	0.1973E-04
29.0	0.170	0.50	0.0000	0.5262E-04	0.0037	0.0000	0.1973E-04
30.0	0.170	0.50	0.0000	0.5262E-04	0.0068	0.0000	0.1973E-04
31.0	0.175	0.60	0.0000	0.6314E 04	0.1203	0.0000	0.268E-04
34.0	0.180	0.60	0.0000	0.6314E-04	0.1317	0.0000	0.268E-04
35.0	0.170	0.60	0.0000	0.6314E-04	0.354	0.0000	0.268E-04
37.0	0.175	0.60	0.0000	0.6314E 04	0.1430	0.0000	0.268E-04
38.0	0.180	0.60	0.0000	0.6314E-04	0.468	0.0000	0.268E-04
40.0	0.185	0.60	0.0000	0.6314E 04	0.544	0.0000	0.268E-04
41.0	0.220	0.70	0.0000	0.7367E 04	0.585	0.0000	0.268E-04
42.0	0.810	0.80	0.0000	0.8192E 04	0.1632	0.0000	0.3132E-04
43.0	0.850	1.00	0.0049	0.9898E-04	0.0086	0.0000	0.3132E-04
44.0	0.860	1.10	0.1029	0.1075E-04	0.1743	0.0000	0.4248E-04
45.0	0.870	1.10	0.142	0.154E 04	0.8	0.0000	0.4248E-04
46.0	0.885	1.40	0.1032	0.1508E 04	0.1888	0.0000	0.4248E-04
47.0	0.895	1.50	0.1543	0.1509E 04	0.969	0.0000	0.5340E-04
48.0	0.900	1.60	0.214	0.1441E 04	0.2054	0.0000	0.5340E-04
49.0	0.900	1.70	0.214	0.1531E-04	0.2142	0.0000	0.6045E-04
50.0	0.900	2.00	0.214	0.1801E 04	0.2242	0.0000	0.6045E-04
51.0	0.895	2.10	0.1943	0.1916E-04	0.254	0.0000	0.7554E-04
52.0	0.890	2.30	0.1782	0.2124E-04	0.2475	0.0000	0.7554E-04

53.0	0.89F	2.3C	0.1943	0.2099E=0-	0.2602	94.0679	0.87.7E=04
54.0	0.890	2.4C	0.182	0.2217E=0-	0.273	98.749	0.9.26E=04
55.0	0.89F	2.4C	0.1943	0.2190E=0-	0.286	103.529	0.9C96E=04
56.0	0.900	2.4C	0.214	0.2162E=0-	0.294	108.2496	0.9065E=04
57.0	0.89F	2.3C	0.1943	0.2099E=0	0.3122	112.870	0.8717E=04
58.0	0.890	2.2C	0.182	0.2054E=0	0.3246	117.357	0.8.6E=04
60.0	0.88F	2.2C	0.1832	0.2055E=0	0.349	126.2183	0.8.9.04
61.0	0.885	2.10	0.1822	0.1962E=0-	0.36	130.5753	0.8C.0.04
62.0	0.88-	2.0C	0.1832	0.1868E=0-	0.3726	134.7296	0.7628E=04
64.0	0.880	1.9C	0.192	0.1795E=0	0.3946	142.0713	0.7268E=04
66.0	0.88F	1.8C	0.1832	0.168E=0	0.4.54	147.27	0.6866E=04
65.0	0.885	1.7C	0.1832	0.1588E=0-	0.4449	150.8707	0.6484E=04
72.0	0.88F	1.60	0.1832	0.1495E=03	0.4726	152.8	0.6103E=04
74.0	0.885	1.5C	0.1832	0.140E=0-	0.4900	157.69	0.572E=04
76.0	0.880	1.4C	0.192	0.1322E=0-	0.5063	163.0705	0.5355E=04
78.0	0.880	1.3C	0.192	0.1227E=0-	0.526	168.5954	0.4973E=04
80.0	0.880	1.2C	0.192	0.1135E=0-	0.5358	177.88	0.4590E=04
81.0	0.880	1.10	0.192	0.1038E=0	0.5423	186.77	0.4208E=04
82.0	0.880	1.0C	0.192	0.9439F=04	0.5482	192.38	0.3825E=04
83.0	0.875	1.0C	0.163	0.9531E=0	0.5539	197.85	0.3835E=04
84.0	0.875	0.90	0.163	0.8578E=04	0.5594	202.7457	0.3452E=04
85.0	0.870	0.8C	0.142	0.7693E=0-	0.5642	204.0.06	0.3070E=04
87.0	0.865	0.8C	0.132	0.7755E=04	0.5735	207.761	0.3083E=04
92.0	0.865	0.70	0.132	0.6787E=04	0.5953	215.7492	0.2598E=04
94.0	0.860	0.70	0.1029	0.6858E=04	0.6035	218.2019	0.2703E=04
101.0	0.860	0.60	0.1029	0.5861E=04	0.6302	227.8469	0.2317E=04
110.0	0.860	0.6C	0.1029	0.5861E=04	0.6618	239.2901	0.2317E=04
113.0	0.855	0.6C	0.0935	0.5901E=04	0.672	243.1177	0.2322E=04
115.0	0.850	0.60	0.049	0.5939E=04	0.6795	245.6804	0.2320E=04
116.0	0.84F	0.6C	0.0770	0.5973E=04	0.683	246.9784	0.2330E=04
118.0	0.840	0.5C	0.0698	0.5004E=04	0.6897	249.3598	0.1944E=04
120.0	0.830	0.50	0.072	0.5050E=04	0.6957	251.5408	0.1949E=04
130.0	0.825	0.5C	0.018	0.5070E=04	0.726	262.574	0.1952E=04
131.0	0.820	0.5C	0.068	0.5088E=04	0.729	263.6192	0.1954E=04
132.0	0.81F	0.50	0.023	0.5105E=04	0.7322	264.7248	0.1956E=04
135.0	0.810	0.5C	0.082	0.5120E=04	0.744	268.059	0.1957E=04
137.0	0.80F	0.5C	0.045	0.5135E=04	0.7475	270.2702	0.1959E=04
138.0	0.800	0.5C	0.011	0.5146E=04	0.7506	271.5912	0.1960E=04
144.0	0.790	0.50	0.0253	0.5167E=04	0.7691	278.1033	0.1963E=04
145.0	0.785	0.50	0.028	0.5177E=04	0.7723	279.2253	0.1904E=04

147.0	0.780	0.50	0.006	0.5185E-04	0.785	281.4722	0.1905E-04
148.0	0.765	0.50	0.054	0.5205E-04	0.7810	282.6002	0.1907E-04
149.0	0.755	0.50	0.022	0.5215E-04	0.7847	283.7307	0.1968E-04
150.0	0.745	0.50	0.055	0.5225E-04	0.7819	284.8622	0.1969E-04
151.0	0.745	0.50	0.099	0.5225E-04	0.7910	285.9967	0.1969E-04
152.0	0.730	0.50	0.072	0.5235E-04	0.7942	287.1233	0.1970E-04
153.0	0.735	0.50	0.080	0.5235E-04	0.7973	288.2566	0.1970E-04
154.0	0.720	0.50	0.055	0.5240E-04	0.8004	289.4033	0.1971E-04
155.0	0.715	0.50	0.053	0.5242E-04	0.8036	290.5295	0.1971E-04
156.0	0.695	0.50	0.035	0.5249E-04	0.8067	291.6775	0.1972E-04
157.0	0.660	0.50	0.016	0.5256E-04	0.8099	292.8259	0.1973E-04
158.0	0.290	0.50	0.000	0.5262E-04	0.8130	293.9578	0.1973E-04
159.0	0.280	0.50	0.000	0.5262E-04	0.8162	295.0993	0.1973E-04
160.0	0.275	0.50	0.000	0.5262E-04	0.8193	296.2408	0.1973E-04
161.0	0.250	0.50	0.000	0.5262E-04	0.8225	297.3823	0.1973E-04
TOTAL LOSS=							
TOTAL LOSS=							

TOTAL LOSS= 0.8225
TOTAL LOSS= 0.3255

5
 RATUR = 935.0000
 YTL C.LL TEMPERATURE = 826.0000
 T = -2608E-04
 HEIGHT OF THE CRF = 0.9900

TIME (MINS)	VOLTS	DEL H (GMS)	CC FRACTION	INS.C LOSS (CMS/SEC)	CUM.C LOSS (CMS)	PCT O LOSS	INS.C LOSS (GMS/SEC)
2.0	0.120	4.50	0.000	0.205E-04	0.004	0.489	0.754E-05
4.0	0.125	4.00	0.000	0.602E-04	0.006	1.477	0.625E-05
5.0	0.125	2.10	0.000	0.1288E-04	0.005	1.595	0.4829E-05
7.0	0.125	2.50	0.000	0.1039E-04	0.005	2.090	0.3855E-05
9.0	0.125	2.40	0.000	0.9970E-04	0.007	2.527	0.3759E-05
12.0	0.130	2.20	0.000	0.8724E-04	0.008	3.127	0.3272E-05
13.0	0.130	2.90	0.000	0.7893E-04	0.005	3.660	0.2960E-05
17.0	0.130	1.60	0.000	0.6647E-04	0.004	3.974	0.2493E-05
20.0	0.135	1.50	0.000	0.6231E-04	0.003	4.180	0.2357E-05
22.0	0.140	1.30	0.000	0.5401E-04	0.003	4.635	0.2025E-05
25.0	0.145	0.90	0.000	0.3739E-04	0.003	4.928	0.1402E-05
27.0	0.140	1.00	0.000	0.4154E-04	0.004	5.097	0.1558E-05
30.0	0.150	0.80	0.000	0.3323E-04	0.005	5.380	0.1246E-05
34.0	0.155	0.90	0.000	0.3739E-04	0.005	5.645	0.1402E-05
38.0	0.155	0.80	0.000	0.3323E-04	0.005	5.943	0.1246E-05
41.0	0.155	0.90	0.000	0.3739E-04	0.005	6.169	0.1402E-05
45.0	0.160	1.00	0.000	0.4154E-04	0.005	6.597	0.1558E-05
50.0	0.155	1.00	0.000	0.3739E-04	0.005	6.948	0.1246E-05
52.0	0.160	1.20	0.000	0.4985E-04	0.006	7.444	0.1869E-05
55.0	0.160	1.20	0.000	0.4985E-04	0.006	7.894	0.1869E-05
67.0	0.140	1.20	0.000	0.4985E-04	0.006	8.745	0.1869E-05
70.0	0.140	1.30	0.000	0.5401E-04	0.005	9.079	0.2025E-05
76.0	0.145	1.30	0.000	0.5401E-04	0.005	9.775	0.2025E-05
80.0	0.150	1.40	0.000	0.5816E-04	0.005	10.974	0.2181E-05
92.0	0.145	1.50	0.000	0.5816E-04	0.005	12.095	0.2181E-05
100.0	0.145	1.50	0.000	0.6231E-04	0.005	12.740	0.2357E-05
110.0	0.145	1.50	0.000	0.6231E-04	0.005	14.076	0.2357E-05
115.0	0.155	1.70	0.000	0.7062E-04	0.004	14.781	0.2648E-05
127.0	0.155	1.70	0.000	0.7062E-04	0.004	16.603	0.2648E-05
135.0	0.155	1.50	0.000	0.6231E-04	0.005	17.401	0.2357E-05
145.0	0.155	1.40	0.000	0.5816E-04	0.005	19.050	0.2181E-05

151.0	0.145	1.30	0.0000	0.5401E 02	0.0553	9.7507	0.2025E 02
155.0	0.150	1.20	0.0000	0.4985E 02	0.0566	90.4956	0.1869 -05
165.0	0.145	1.20	0.0000	0.4985E 02	0.0595	2.262	0.1859 -05
171.0	0.150	1.10	0.0000	0.4570E 02	0.0623	2.8770	0.1714E 02
180.0	0.150	1.10	0.0000	0.4570E 02	0.0638	22.7548	0.1714E 02
185.0	0.155	0.90	0.0000	0.3739E 02	0.0650	23.2046	0.1402E 05

TOTAL 0 LGSS= 0.0650
 TOTAL C LOSS= 0 C244

EXPERIMENT NO. = 972.0000
 REACTION TEMPERATURE = 818.5000
 SOLID ELECTROLYTE CELL TEMPERATURE = 818.5000
 CAPILLARY CONST = 0.6608E C3
 WEIGHT OF THE CRF = 1.0025

TIME (MINS)	VOLTS	DEL H (GMS)	CC FRACTION	INS.O LOSS (CMS/SEC)	CUM C LOSS (CMS)	PCT.O LOSS	INS.C LOSS (GMS/SEC)
3.0	0.150	0.80	0.0000	0.849E 0	0.00	50.0	0.357 -0.0
4.0	0.150	0.70	0.0000	0.7367E 0	0.0040	2303	0.276 -0.0
5.0	0.145	0.70	0.0000	0.7367E 0	0.0193	6.7803	0.2763 0.0
6.0	0.145	0.60	0.0000	0.6314E 0	0.0274	9.270	0.268 -0.0
7.0	0.150	0.60	0.0000	0.6314E 0	0.0274	9.5704	0.268 0.0
8.0	0.145	0.60	0.0000	0.6314E 0	0.0309	0.9018	0.268 -0.0
9.0	0.130	0.60	0.0000	0.6314E 0	0.0347	2.242	0.2368 0.0
10.0	0.120	0.60	0.0000	0.6314E 0	0.0385	3.576	0.2208 0.0
11.0	0.110	0.60	0.0000	0.6314E 0	0.0422	4.920	0.197 -0.0
12.0	0.110	0.50	0.0000	0.5262E 0	0.0527	8.5843	0.197 -0.0
13.0	0.110	0.50	0.0000	0.5262E 0	0.0717	15.265	0.197 -0.0
14.0	0.110	0.50	0.0000	0.5262E 0	0.0840	9.770	0.197 -0.0
15.0	0.110	0.50	0.0000	0.5262E 0	0.0906	9.884	0.197 -0.0
16.0	0.110	0.50	0.0000	0.5262E 0	0.0958	3.05	0.197 -0.0
17.0	0.110	0.50	0.0000	0.5262E 0	0.1000	25.2708	0.197 -0.0
18.0	0.110	0.50	0.0000	0.5262E 0	0.1064	17.5025	0.197 -0.0
19.0	0.110	0.50	0.0000	0.5262E 0	0.1222	13.0656	0.197 0.0
20.0	0.110	0.50	0.0000	0.5262E 0	0.1338	54.1950	0.197 0.0
21.0	0.110	0.50	0.0000	0.5262E 0	0.160	6.4206	0.197 0.0
22.0	0.110	0.50	0.0000	0.5262E 0	0.1664	18.6453	0.197 0.0
23.0	0.110	0.50	0.0000	0.5262E 0	0.1727	60.8720	0.197 0.0
24.0	0.110	0.50	0.0000	0.5262E 0	0.1759	1.9848	0.197 0.0
25.0	0.110	0.50	0.0000	0.5262E 0	0.1880	16.455	0.197 0.0
26.0	0.110	0.50	0.0000	0.5262E 0	0.1980	69.7756	0.197 0.0
27.0	0.110	0.50	0.0000	0.5262E 0	0.206	74.2200	0.197 0.0
28.0	0.110	0.50	0.0000	0.5262E 0	0.210	17.565	0.197 0.0
29.0	0.110	0.50	0.0000	0.5262E 0	0.213	78.7800	0.197 0.0
30.0	0.110	0.50	0.0000	0.5262E 0	0.2500	88.4	0.2560 0.0
31.0	0.110	0.50	0.0000	0.5262E 0	0.2614	92.1476	0.2560 0.0
32.0	0.110	0.50	0.0000	0.5262E 0	0.2801	98.856	0.2560 0.0
33.0	0.110	0.50	0.0000	0.5262E 0	0.2879	101.2904	0.2560 0.0

108.0
109.0
110.0

0.135
0.140
0.155
0.175
0.400
0.760
0.900
0.810
0.620
0.815
0.825
0.830
0.820
0.805
0.780
0.685
0.185
0.160
0.150
0.145

0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000
0.000

0.6214E 04
0.7307E 04
0.7567E 04
0.7307E 04
0.7367E 04
0.7296E 04
0.7209E 04
0.7174E 04
0.7262E 04
0.7155E 04
0.7048E 04
0.7078E 04
0.7130E 04
0.7192E 04
0.7262E 04
0.6302E 04
0.6324E 04
0.5262E 04
0.5262E 04
0.5262E 04

0.295
0.299E
0.008
0.029
0.315
0.027
0.026
0.020
0.0347
0.039
0.0476
0.05603
0.03646
0.03689
0.03732
0.03775
0.038
0.03845
0.03877
0.03909

0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.11
0.12
0.13
0.14
0.15
0.16
0.17
0.18
0.19
0.20
0.21
0.22
0.23

0.2368E 04
0.2762E 04
0.2763E 04
0.2763E 04
0.2763E 04
0.2763E 04
0.2755E 04
0.2755E 04
0.2745E 04
0.2762E 04
0.2739E 04
0.2727E 04
0.2750E 04
0.2756E 04
0.2743E 04
0.2751E 04
0.2367E 04
0.2368E 04
0.1973E 04
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0.1973E 04

TOTAL 0 LOSS= 0.3909
TOTAL 0 LOSS= 0.2470

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1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

APPENDIX - III

SAMPLE COMPUTER PRINTOUTS ASSUMING
 $\text{CO}-\text{CO}_2-\text{C}_2$ EQUILIBRIUM TO BE "FROZEN"
AT REACTION TEMPERATURE.

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APPENDIX -IV

Tables of the results of the experiments

Experiment No. 1

Iron ore powder + graphite

Reaction temp. = 1047°C

Time min	Fe reduction	$\frac{w_c}{w_o}$ if gms/gms-sec $\times 10^4$
2.0	5.00	3.4896
3.0	9.44	2.7509
4.0	17.84	15.4356
5.0	29.03	9.1696
7.0	46.32	7.9213
10.0	66.50	5.6546
12.0	76.60	4.1263
15.0	86.40	2.2413
19.0	93.80	1.5283
29.0	100.00	1.3500

Experiment No. 2

Iron ore powder + graphite

Reaction temperature = 1042° C.

Time min	per cent reduction	$\frac{w_{O_2}}{w_{CO_2}}$ gas/g ore - gas $\times 10^{+4}$
2.0	5.55	4.8143
3.0	10.82	4.3022
4.0	18.14	13.5211
6.0	39.12	10.9347
7.0	47.95	9.1677
9.0	62.12	7.1703
12.0	77.68	4.6863
15.0	86.73	2.6689
19.0	93.89	1.7157
23.0	100.00	1.7670

Experiment No. 3

Iron ore powder + graphite

Reaction temperature = 1013°C

Time min	Fe reduction	$v_{c,f}$ gms/gms-sec $\times 10^4$
2.0	2.62	1.6023
7.0	15.06	1.6023
8.0	18.52	2.8009
9.0	23.69	6.8130
12.0	40.17	6.0813
16.0	57.62	4.2140
20.0	70.36	3.2046
28.0	87.64	1.6654
37.0	100.00	1.0598

Experiment No. 4

Iron ore powders graphite

Reaction temperature = 974°C

Time min	per cent reduction	$\frac{w_{\text{Fe}}}{w_{\text{Fe}} + w_{\text{C}}} \times 10^4$
3.0	3.36	0.7169
9.0	10.31	0.5192
23.0	22.91	0.3708
35.0	32.77	0.4203
41.0	35.34	0.5192
45.0	41.7	0.7169
47.0	43.7	0.9147
50.0	47.2	1.2114
55.0	55.2	1.4586
61.0	64.8	1.2608
69.0	75.5	1.0136
80.0	87.2	0.7169
85.0	90.8	0.4944

Experiment No. 5

Iron ore powder + graphite

Reaction temp. = 933°C

Time min	Pct reduction	$w_{c,f}$ gms/gms-sec $\times 10^4$
2.0	0.88	0.4950
12.0	5.66	0.1980
17.0	7.17	0.0990
67.0	15.8	0.0990
115.0	26.7	0.1980
185.0	41.9	0.0990

Experiment No. 6

Iron ore pellets + graphite

Reaction temp = 1054°C

Time min	Pct reduction	$\frac{w_{e,f}}{gms/gms-sec}$ $\times 10^4$
2.0	2.51	2.9982
5.0	12.30	2.1453
9.0	21.18	1.7576
16.0	34.17	1.6283
27.0	51.08	1.5249
37.0	63.30	1.5249
41.0	70.72	1.4474
50.0	81.80	1.1889
62.0	92.33	0.8012
73.0	100.00	0.3102

Experiment No. 7

Iron ore pellets + graphite

Reaction temp. = 1052°C

Time min	per cent reduction	$\frac{w}{A \cdot t}$ gms/gms-sec $\times 10^4$
3.0	8.54	2.5197
5.0	15.10	2.2572
9.0	25.70	1.3911
15.0	35.10	1.2335
21.0	44.40	1.1549
31.0	57.5	1.0761
45.0	75.3	1.0761

Experiment No. 8

Iron ore pellets + graphite

Reaction temp. = 1019°C

Time min	pct reduction	$\frac{w_{\text{Fe}}}{w_{\text{Fe}} + w_{\text{C}}}$ gms/gms-sec $\times 10^4$
2.0	3.73	1.8583
3.0	6.70	1.8844
9.0	23.00	1.0325
15.0	37.60	1.1100
34.0	44.30	1.0325
48.0	70.76	1.0325
58.0	90.50	1.2132

Experiment No. 9

Iron ore pellets + graphiter

Reaction temp. = 972°C

Time min	wt reduction	$\frac{w}{t}$ gms/gms. sec $\times 10^4$
3.0	2.72	1.1945
8.0	8.32	0.8829
27.0	25.2	0.7531
64.0	56.7	0.7531
90.0	83.0	1.0647
97.0	90.0	0.9348
110.0	100.0	0.7531

Experiment No. 10

Pure Fe_2O_3 + graphite Reaction temp. = 955°C

Time min	pet reduction	wt $\text{W}_{\text{C},f}$ gas/gms. sec $\times 10^4$
4.0	2.04	0.5930
18.0	12.35	0.5930
31.0	18.56	0.3385
79.0	32.27	0.3385
82.0	34.00	0.7638
84.0	35.13	1.3368
86.0	38.93	2.0359
94.0	49.68	1.6985
104.0	60.15	1.3368
119.0	71.46	0.8475
166.0	89.07	0.3385
202.0	100.00	0.2546

Experiment No. 11

Pure Fe_2O_3 graphite

Reaction temp. = 938°C .

Time min	per cent reduction	$\frac{w}{a} \frac{d}{f}$ gm ² /gm ² -sec $\times 10^4$
3.0	1.24	0.4343
27.0	11.38	0.2626
69.0	20.92	0.1758
97.0	25.00	0.0862
133.0	30.73	0.2620
135.0	31.72	0.6101
141.0	38.55	1.3064
167.0	61.79	0.8687
213.0	85.00	0.3482
254.0	100.00	0.2620

C) Interpretation of ore-graphite powder mixture and pure

Fe_2O_3 - graphite powder mixture:

The $\dot{w}_{a,f}$ Vs pct reduction curves for ore-graphite powder mixture (fig 6-1) and (6-2) as well as Fe_2O_3 -graphite powder mix (fig 6-4) show the two stage behaviour as reported earlier by Otsuka and kunii (fig. 1-3) . The rates of the second stage are higher compared to those in the first stage. The rates do not become zero at 100 pct, reduction because of experimental errors.

Otsuka and kunii explain this enhancement of rate in the second stage as due to catalytic effect of reduced iron on the rate of gasification reaction. A confirmation of their contention was that they found the activation energy to be high (55-75) Kcal in the first stage and low (15-23 kcal) in the second stage.

Fig 6-5 shows $\log w_{a,f}$ Vs $\frac{1}{T}$ plots. For ore-graphite mixture, activation energy (E) = 105 Kcal/mole at 10 pct. reduction (first stage) and E = 70 Kcal/mole for 60 pct. reduction (second stage). Noting that the activation energy of uncatalysed gasification reaction is 80-90 Kcal/mole, the following points emerge.

1. The reaction between ore and graphite powder is controlled by the rate of gasification.
2. Catalytic enhancement of rate, presumably by reduced iron is occurring in the second stage.

Fig. 6-5 also shows that the rates in ore graphite are not substantially different from those in Fe_2O_3 -graphite system.

This is expected if gasification reaction is rate controlling and therefore confirms the above conclusion no. 1.

For Fe_2O_3 -graphite reaction, no attempt was made to determine the activation energy since there were data only at two temperatures.

D) Interpretation for ore-pellet-graphite powder mixtures:

This differed from the ore powder-graphite powder mixture in the following respects

1. The $w_{c,f}$ Vs pct reduction curves show one peak at less than 10 pct. reduction. Above 30 pct reduction the rates are steady and lower. Therefore these are marked by absence of the enhancement at the second stage as in the case with the powder mixture.
2. Activation energy is lower (34-Kcal/mole for 20 pct. reduction and 17 Kcal/mole for 60 pct. reduction) compared to those with powder mixtures.
3. The rate at 60 pct reduction is substantially less compared to the same for powder mixture.
4. The rates at 20 pct reduction are less at higher temperatures but more at lower temperatures compared to those for powder mixture.

The lowering of the rate may very well be explained as due to less contact surface area in the pellet graphite case. The absence of an enhanced second stage may be due to any of the followings:

1. Gasification reaction not controlling the rate
2. The gasification reaction is controlling, but either catalyzed or uncatalyzed throughout. The uncatalyzed case is ruled out because of the low activation energy.

Lowering of the activation energy may be due to:

1. Ore reduction rate controlling
2. Gasification rate controlling, but catalyzed throughout the reduction period.
3. Long range diffusion in graphite rate controlling.

In order to clarify it further literature data on rate of reduction of iron oxides by carbon monoxide was picked up from the investigations in the past.

Bicknese and clerke (18) prepared synthetic FeO (-12 to + 16 mesh) from pure Fe_2O_3 and Fe, then compacted this FeO and subjected it to reduction in CO in packed bed by the thermobalance^a technique. They could fit their rate data with the following equations:-

$$(1-(1-f)^{1/3})/t = (4.3 \exp(-\frac{13,800}{RT}) \times (\frac{C_e - C}{C_e}) \quad (6.11)$$

Where f = fractional reduction

t = time in minutes

C_e = equilibrium concentration of CO_2 in equilibrium with Fe_3O_4 -Fe.

C = actual concentration of CO_2 in the gas stream

Smith and Mckewan (15) studied the kinetics of reduction of hematite ore pellets of 1.5 - 1.9 cm diameter and porosity. @x 0.21 in pure CO and CO-H₂ gas mixture by single pellet thermobalance technique. They fitted their rate equation as:

$$K = \frac{R_o d_o (1 - (1 - f)^{1/3})}{t} \quad \dots\dots (16-12)$$

Where K = rate constant in mg/cm²/min

R_o = original pellet radius

d_o = oxide density

For pure CO, $K = \text{Bexp.}^{-\left(\frac{8500}{RT}\right)}$ and values were 14.9 at 955°C and 18.2 at 1038°C.

Noting that in this investigation, pellet diameters were approximately 5 mm, porosity approximately 30 pct (assumed) and that there were 5 pellets in each experiment, some sample calculations were made as follows.

- i) Time taken to alter f from 0.4 to 0.8 was calculated from the equations of Bicknese and clerk as well as Smith and Mckewan. The gas was taken as pure CO.
- ii) Assuming CO/CO₂ ratio to be 4:1, carbon loss rate and hence $w_{o,f}$ were calculated.
- iii) The corresponding loss of oxygen was calculated.

Results of such calculations are presented in fig. 6-5. It may be noted that the calculated rates are fairly close to those obtained from experiments. Low activation energy is also explained. Hence it is concluded that the ore reduction stage is controlling the rate of reduction between ore pellet and graphite, if not fully, at least partially.

CHAPTER VII

SUMMARY AND CONCLUSIONS:

- 1) Oxygen sensor was fabricated using CSZ as solid electrolyte.
- 2) Sensor performance was tested in O_2-N_2 mixtures (oxygen conc. in the range 1 pct- 10 pct) and air in the temperature range of $1050^{\circ}K - 1250^{\circ}K$. Data obtained fall within 20 pct of those estimated from flow meter reading. In most of the cases the error was positively which indicates that the source of error may be poor electrode contact. Also at low oxygen concentration the scatter of flowmeter may be the other source of error.
- 3) Using the flowmeter and above sensor, kinetics of reduction of iron ore by carbon was investigated. -325 mesh powder and 5 mm. sintered pellets of iron ores from Rajhara mines (Durg) was used. Some experiments were also performed using pure Fe_2O_3 powder. The temperature range of the experiments was $925^{\circ}C - 1050^{\circ}C$.
- 4) Computer calculations were executed to obtain CO fraction, pct. reduction, cumulative carbon and oxygen wt. loss, and instantaneous rates of carbon and oxygen removal.
- 5) Results indicated that the $CO-CO_2-O_2$ equilibrium, Corresponding

to the reaction temperature remained 'frozen' even in the oxygen sensor. Therefore further calculations were done by assuming the equilibrium to be frozen. Some correction procedures were used to get the specific rate of carbon weight loss ($\dot{W}_{c,f}$) and pct. reduction.

- 6) The ore powder-graphite powder mixture as well as pure Fe_2O_3 , graphite mixture show two-stage behavior. Second stage show enhanced rate of reduction presumably by catalysis. Activation energy for the reaction is high. Hence gasification is concluded to be rate controlling.
- 7) The ore pellets-graphite mixtures show low activation energy and reduction rates are also lower. Assuming ore reduction stage to be rate controlling, rates of ore reduction in pure CO were calculated based on the literature information. These calculations are in good agreement with the results calculated from the experimental data. This indicates that the ore reduction step is at least partially rate controlling.

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APPENDIX V

THEORETICAL CALCULATIONS FOR THE REDUCTION

OF PELLETS ASSUMING REDUCTION STAGE TO BE

RATE CONTROLLING

Weight of the ore pellets = 1 gm.

Weight of the graphite \approx 0.4 gm.

$W_O = \Delta f \times$ Weight of oxygen in ore pellet

$$= \Delta f \times 0.263$$

Consider the time interval during which fractional reduction (f) changed from 0.8 to 0.4.

f	1-f	(1-f) ^{1/3}	$\Delta(1-f)^{1/3}$	ΔW_O gms.
0.4	0.6	0.843	0.238	0.113
0.8	0.2	0.585		

$$\begin{aligned} \dot{W}_O &= \frac{\Delta W_O}{\Delta t} = \frac{\Delta W_O}{\Delta (1-f)^{1/3}} \times \frac{\Delta (1-f)^{1/3}}{\Delta t} \\ &= 0.498 \times \frac{(1-f)^{1/3}}{t} \end{aligned} \quad (1)$$

Thus by knowing $\frac{(1-f)^{1/3}}{t}$ from literature data, \dot{W}_O can be calculated.

Now assume CO/CO₂ ratio (γ) = 4/1

$$\text{Then, } \frac{W_C}{W_O} = \frac{12}{32} \times \frac{2(\gamma+1)}{\gamma+2} = \frac{12}{32} \times \frac{10}{6} = \frac{5}{8} \quad (2)$$

$$\text{Hence } \dot{W}_C = \frac{5}{8} \dot{W}_O$$

$$\text{It is already stated that } \dot{W}_{C,f} = \frac{\dot{W}_C}{\text{original wt. of carbon}} \quad (4)$$

1) Calculations assuming Bicknese and Clarke relationship to be valid.

$$\frac{1-(1-f)^{1/3}}{t} = 4.3 \exp. \left(\frac{-13,800}{RT} \right) \times \frac{C_g - C}{C_g}$$

Since the gas is assumed to be pure CO_2 , $C = 0$.

$$\therefore \frac{C_g - C}{C_g} = 1$$

So at the reaction temperatures, corresponding $\frac{1-(1-f)^{1/3}}{t}$

values are known, from which \dot{W}_O , \dot{W}_C and $\dot{W}_{C,f}$ can be calculated.

Thus the calculated results are:

Expt. No.	Temp. °K	$\frac{\Delta(1-f)^{1/3}}{\Delta t (\text{sec}^{-1})}$	$\dot{W}_O \times 10^4$ gms/sec.	$\dot{W}_C \times 10^4$ gms/sec.	$\dot{W}_{C,f} \times 10^4$ (sec ⁻¹)
6	1327	4.10	1.80	1.125	2.812
7	1325	4.06	1.79	1.12	2.78
8	1292	3.31	1.45	0.906	2.26
9	1245	2.72	1.105	0.69	1.72

2) Calculations assuming Smith and McKewen's equation to be valid.

$$K = \frac{R_p d_p (1-(1-f)^{1/3})}{t}$$

R_p = radius of the pellets = 0.25 cm.

d_p = density of the pellets = 3.7 gms/cc

(assuming 30% porosity).

Values of K are 14.9 and 18.2 mg/cm²/min at 955°C and 1038 °C respectively.

From this data $\frac{\ln(1-f)^{1/3}}{t}$ can be calculated at 955 °C and 1038 °C and then \dot{w}_O , \dot{w}_C and $\dot{w}_{c,f}$ have been obtained as shown earlier.

Thus the results obtained are :

Temp. °K	$\frac{\ln(1-f)^{1/3}}{t}$ (Sec ⁻¹)	$\dot{w}_O \times 10^4$ gms/sec	$\dot{w}_C \times 10^4$ gms/sec.	$\dot{w}_{c,f} \times 10^4$ sec ⁻¹
1228	2.68	1.175	0.734	1.835
1311	3.28	1.438	0.899	2.247

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